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Enhanced conductivity in polyanion-containing polybenzimidazoles. Improved materials for proton-exchange membranes and PEM fuel cells

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Abstract

In an effort to develop improved Proton Exchange Membranes for Polymeric Fuel cells two different forms of polyanion inclusion in poly(2,5-benzimidazole) (ABPBI) have been carried out. Namely by (i) sulfonation of pre-formed polymer membranes and (ii) by addition of inorganic phosphomolybdic acid to form hybrid ABPBI-PMO₁₂ membranes. In both cases we have detected an increased proton conductivity of the resulting membranes, associated to an enhanced capacity of the polyanion-modified materials to uptake phosphoric acid (in comparison with previously known ABPBI or even commercial PBI membranes). These new membranes are stable up to 200 °C and feature high conductivities at these temperatures, which makes them promising candidates for higher-temperature PEM Fuel Cells.

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Keywords: Polybenzimidazole; PBI; ABPBI; Sulfonated polybenzimidazole; Polymer electrolyte; PEMFC membranes; Heteropoly acid; Phosphomolybdic; PMO₁₂

1. Introduction

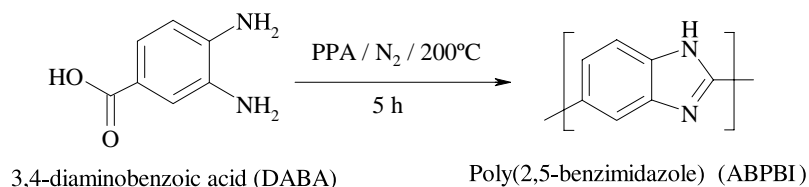
The present technology of polymer electrolyte membrane fuel cells (PEMFC) is based on the proton conductivity of perfluorosulfonated membranes, with Nafion® as the most extensively studied example. But Nafion membranes limit the PEMFCs in two main ways. First, the high cost of perfluorinated polymers increases the final price of the stacks. The other key – and expensive-components of a cell are the Pt-based electrodes. These electrodes are very sensitive to CO impurities present in the hydrogen commonly used as fuel and force the use of ultra pure hydrogen, thus raising the cost of this technology. And yet, with working temperatures above 150–165 °C the dreaded poisoning of the Pt catalyst could be reduced. This

would allow the use of not so pure hydrogen as fuel in PEMFC. But Nafion and other perfluorinated polymers only perform properly below 100 °C, because above that temperature the membrane dehydrates and the proton conductivity decays sharply. That is why so much effort is presently devoted to the development of alternative inexpensive materials for the fabrication of PEM membranes able to stand higher temperatures, sustaining high proton conductivities above 150 °C.

Polybenzimidazoles constitute a promising new group of materials both for their low-cost and high working temperature. The key for the proton conduction in polybenzimidazole-based membranes is their impregnation with phosphoric acid. Indeed switching from water-impregnated to phosphoric acid-impregnated materials allows working temperatures of up to 180–200 °C and intense development efforts are being made to put these alternative membranes to work. PBI, the first commercially available of these polymers has been extensively studied in this respect [1–11], although

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Scheme 1. Synthesis of ABPBI.

other derivatives such as poly(2,5-benzimidazole) (ABPBI, Scheme 1) are equally promising. H_3PO_4 -PBI membranes are able to work at temperatures up to 200 °C without humidification, and allow the use of H_2 with up to 3% of CO impurities with only a small power loss [9]. Phosphoric acid doped PBI has been used in PEMFC fed with different fuels [8,9,12–17], whereas ABPBI has also been shown to form good membranes and perform as PEM upon impregnation with phosphoric acid [3,18]. H_3PO_4 -ABPBI membranes have been used successfully as electrolyte in supercapacitors [19] and H_2/O_2 fuel cells at temperatures up to 180 °C [20]. However polybenzimidazole membranes also need improvement, since they could benefit from higher conductivities and it has been detected that they can suffer phosphoric acid leaking upon extended use under their harsh working conditions.

We have recently carried out some work on polybenzimidazole membranes [11,21–23] with special emphasis on ABPBI (Scheme 1) and have conducted preliminary experiments in order to modify and improve them in several ways. We report here the materials resulting from the integration of different polyanions (either inorganic heteropolyanions or sulfonated derivatives) in an attempt to develop modified polybenzimidazole membranes with improved performances both from the point of view of their conductivity and long-term endurance.

Heteropoly acids (HPAs) were considered as ideal additives for PBIs since they constitute a whole family of solid acids, with a thermal stability much higher than phosphoric acid doped PBI. In addition, we have had experience integrating these nanometric inorganic clusters within conducting polymers (i.e. phosphomolybdic acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, denoted PMo_{12} , in polyaniline, polypyrrole) to yield electroactive hybrid organic–inorganic materials [19,24–26]. Very recently, the doping of commercial PBI with heteropolyacids (in particular $\text{H}_3\text{PW}_{12}\text{O}_{40}$, phosphotungstic acid, denoted PW_{12}) has been studied, but the properties of the these hybrid materials (in particular their conductivities) were not judged good enough to be used as membranes in PEMFCs [27–30].

In addition to hybrid organic–inorganic membranes with HPAs, our second choice for the loading of acidic groups in polybenzimidazoles was sulfonation. We have been successful in preparing both types of materials,

sulfonated ABPBI and PW_{12} or PMo_{12} -ABPBI hybrid polymers, as well as in fabricating membranes from them, and report here these synthetic efforts and the characterization of the resulting materials, with special emphasis on the thermal stability and proton conductivity of the novel membranes upon impregnation with phosphoric acid. Our results show that polyanion integration in polybenzimidazoles leads to an increase in phosphoric acid uptake and retention and a consequent improvement in the conductivity of these materials.

2. Experimental

The monomer 3,4-diaminobenzoic acid (DABA) 97% and the solvent methanesulfonic acid (MSA) 99% were obtained from Across Organics and used without further purification. Polyphosphoric acid (PPA) 85% P_2O_5 , 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^{-1} . 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_2SO_4 96%. FTIR spectra of the membranes were recorded on a Shimadzu FTIR-8300 spectrophotometer. 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 as describe before [11,23,31]. Membranes were first heated at 180 °C in order to eliminate the water. By TGA we have seen that absorbed water is eliminated around 100 °C. Conductivity measurements were took while cooling.

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 [21]. Typical inherent viscosity of a 0.5 g dl^{-1}

solution was 2.3–2.4 dl g⁻¹ measured in 96% H₂SO₄ at 30 °C, high enough for casting membranes with good mechanical stability, even when impregnated with high amounts of phosphoric acid, according to the following procedure.

4. Membrane casting

Membranes of ABPBI were prepared by evaporation of a methanesulfonic acid (MSA) solution [18,32]. 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 in water.

PBI membranes were cast from dimethylacetamide solutions as described earlier in many reports [1–10].

Hybrid ABPBI–PMO₁₂ membranes were prepared dissolving ABPBI in MSA as described above, and later adding the desired amount of PMO₁₂. The heterogeneous mixture obtained initially was cast on a glass plate and led to an apparently homogeneous solution upon heating as needed for MSA evaporation at ambient pressure, finally yielding a completely homogeneous membrane. Following this procedure, hybrid membranes can be prepared having a PMO₁₂ content of up to 60% losing a very small amount of the heteropoly acid during the water washing [11]. After the washing of the membranes, the PMO₁₂ content was calculated from elemental analysis data and the water content by TGA. Below 60% PMO₁₂, the amount of the heteropoly does not change after washing in boiling water, losing only a very small amount of PMO₁₂ [11]. We can conclude that the heteropoly acid is not lost during the washing. The membrane used in this work had a composition of ABPBI–45% H₃PMO₁₂O₄₀.

5. Sulfonation of pre-cast APBBI membranes

The sulfonation of performed PBI membranes, by doping in sulfuric acid and heat treating the sulfuric acid membranes, has been described earlier [33–35]. Based on these reports, we have optimized the same procedure for the sulfonation of ABPBI membranes (Scheme 2).

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⁻¹ [4]. The same happens for ABPBI membranes. A 20 μm ABPBI membrane was soaked in H₂SO₄/H₂O 10:90 by volume for 24 h and dried at 100 °C. As ABPBI is *n*·C₇H₄N₂, the doping level was calculated as the molar ratio S/C₇ and S/N₂ from the elemental analysis, finding a composition of ABPBI·0.6 H₂SO₄.

When heating the sulfuric acid doped ABPBI membranes, sulfonation takes place but the membranes become fragile. Since for shorter heating times the membranes were less fragile we have optimized the minimal time needed to sulfonate ABPBI membranes in air at 450 °C. This has been done by following the FTIR evolution of previously cast ABPBI membranes doped in H₂SO₄/H₂O 10:90 v/v for 24 h (Fig. 1). Fortunately, the positions of sulfate and sulfonate bands are quite different and allow to follow their evolution. We have found that for heat treatments over 5 minutes, the intensity of the bands assigned to sulfonate groups

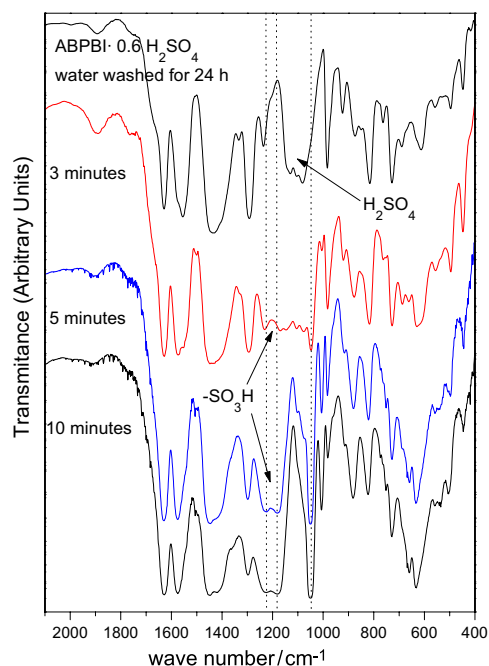
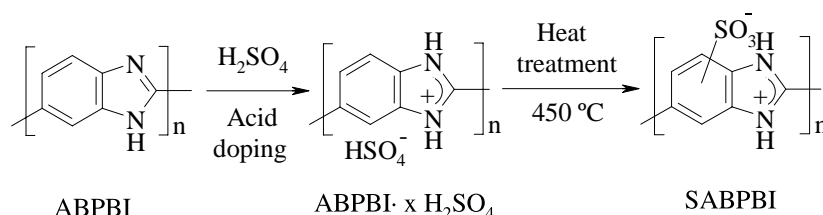


Fig. 1. FTIR of SABPBI. Effect of heat treatment of ABPBI·0.6 H₂SO₄ for different times.



Scheme 2. Sulfonation of ABPBI membranes.

Table 1

Evolution of the FTIR bands in an ABPBI membrane doped in H₂SO₄/H₂O 10:90 by volume for 1 and heat treated in air at 450 °C for 5 min

ν (cm ⁻¹)				Assignment
ABPBI · 0.6 H ₂ SO ₄	ABPBI · 0.6 H ₂ SO ₄ washed 24 h	ABPBI · 0.6 H ₂ SO ₄ 5 min @ 450 °C	ABPBI · 0.6 H ₂ SO ₄ 5 min @ 450 °C washed 24 h	
		1233	1226	-SO ₃ H
		1177	1183	-SO ₃ H
	1141			H ₂ SO ₄
1168	1130			H ₂ SO ₄
1117	1104			H ₂ SO ₄
1082	1080			H ₂ SO ₄
1045		1048	1050	-SO ₃ H

[21,36–39] do not decrease after washing in boiling water for 24 h, whereas the bands assigned to sulfuric acid at lower wave number disappear after that heat treatment (see Fig. 1).

After washing, the sulfonation level was calculated from elemental analyses as the molar ratio S/C₇ and S/N₂. The optimal reaction time, leading to sulfonation with the minimal fragilization is 5 min at 450 °C. Table 1 summarizes the evolution of FTIR spectra of sulfuric acid doped ABPBI membranes heat treated for 5 min.

6. Phosphoric acid impregnation of the membranes

PBI, ABPBI, sulfonated ABPBI (S-ABPBI) and ABPBI-PMO₁₂ membranes were impregnated in the

same H₃PO₄ bath in order to allow meaningful comparisons. Samples of about 2 × 3 cm were cut and immersed in acid solutions of H₃PO₄ 85%/H₂O 70:30 (in volume) for 3 days. The amount of PO₄³⁻ as well as the degree of sulfonation was determined by elemental analysis of C, H, N and S after doping. For ABPBI-PMO₁₂, the amount of acid could not be determined due to the more complex composition of the system (composed of ABPBI, PMO₁₂, H₃PO₄ and some absorbed water). We have confirmed by FTIR that all the characteristic bands of PMO₁₂ are still present and appear at the same wavenumber and with the same intensities upon doping (Figs. 2 and 3), thus confirming that PMO₁₂ is still in the membrane after acid doping [11].

First of all, we noticed that ABPBI absorbs more acid than PBI when doped in the same bath [11]. But in addition, the incorporation of polyanions or the sulfonation increase even further the phosphoric acid uptake of ABPBI.

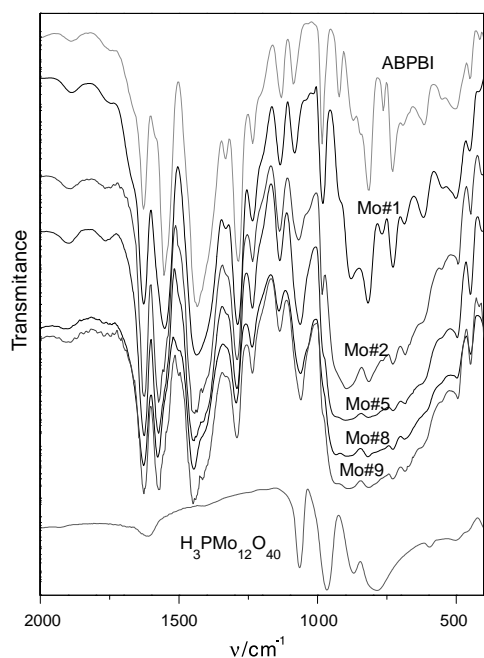


Fig. 2. FTIR spectra of the ABPBI-PMO₁₂ hybrid membranes of different nominal compositions (Mo#1 = 13.4% PMO₁₂, Mo#2 = 45% PMO₁₂, Mo#5 = 60% PMO₁₂, Mo#8 = 70% PMO₁₂, Mo#9 = 80% PMO₁₂). Only compositions below 60% maintain the nominal composition after washing in boiling water 24 h.

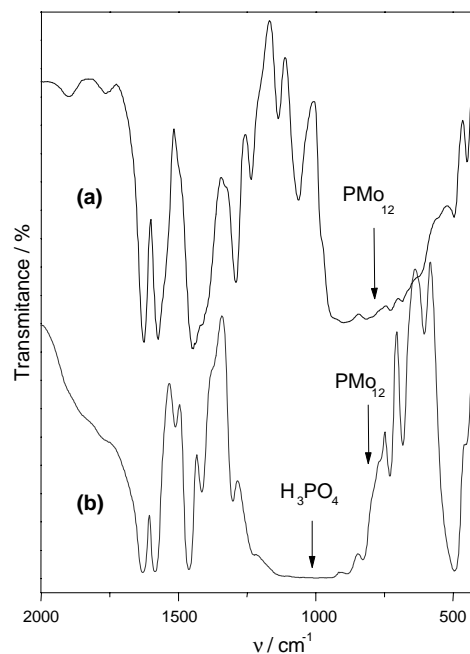


Fig. 3. FTIR of ABPBI-60% PMO₁₂ (a) before and (b) after doping in a H₃PO₄ 85%/H₂O bath (50:50 by volume).

The amount of phosphoric acid uptake was calculated as the number of phosphoric acid molecules per benzimidazole unit. After sulfonation, the sulfonated SAPBI membranes absorb more acid than the non-sulfonated ones when both were soaked in the same bath. The amount of acid present in the ABPBI-PMO₁₂ membranes was not determined, although conductivity measurements (see below) seem to indicate that these inorganic polyanions also enhance the capability of the polymer to incorporate phosphoric acid.

7. Thermal stability and conductivity

Thermogravimetric analyses showed that all the phosphoric doped membranes were stable up to 200 °C. We have measured the conductivity at temperatures below 185 °C. Fig. 4 shows plots of conductivity vs. temperature for PBI, ABPBI, ABPBI-PMO₁₂, and sulfonated SABPBI membranes doped with H₃PO₄. Among them, ABPBI, ABPBI-PMO₁₂, SABPBI were doped in the same bath, but PBI was doped in a more concentrated bath in order to achieve comparable doping levels (in weight %), since it absorbs much less acid than the other membranes. In this way, membranes PBI · 6.7 H₃PO₄ and ABPBI · 2.7 H₃PO₄, were obtained, both with ca. 68% H₃PO₄.

First of all it should be noted that those PBI and ABPBI membranes present very similar conductivities (in agreement with the predominant role of phosphoric acid in that conduction). This confirms ABPBI as a material as good as commercial PBI for fuel cell applications.

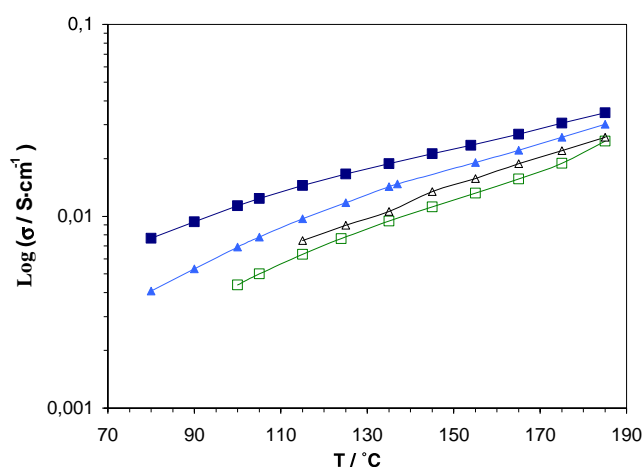


Fig. 4. Conductivity of membranes based on SABPBI (-SO₃H 41%) · 4.6 H₃PO₄ (■), ABPBI · 45% H₃PMO₁₂O₄₀ · xH₃PO₄ (▲), ABPBI · 2.7 H₃PO₄ (□). The three membranes were doped in the same bath (H₃PO₄ 85%/H₂O 70:30 v/v). The conductivity PBI · 6.7 H₃PO₄ (△) is added for comparison, prepared doping in a more concentrated phosphoric acid bath, in order to achieve an acid content similar to ABPBI · 2.7 H₃PO₄.

Table 2

Activation energies of the conductivities of different phosphoric acid doped polybenzimidazoles

Membrane	E_a (kJ mol ⁻¹)
PBI · 6.7 H ₃ PO ₄	26.5
ABPBI · 2.7 H ₃ PO ₄	27.4
ABPBI 45% PMO ₁₂ · xH ₃ PO ₄	25.1
SABPBI 41% -SO ₃ H 4.6 H ₃ PO ₄	18.7

The three ABPBI membranes were doped in the same bath (H₃PO₄ 85%/H₂O 70:30 v/v). The PBI membrane was prepared doping in a more concentrated phosphoric acid bath, in order to achieve an acid content similar to ABPBI · 2.7 H₃PO₄.

Furthermore, the sulfonated SABPBI polymer presents an even higher conductivity. In principle we assign this to the larger amount of acid present in this sample (as we have pointed out, sulfonate groups enhance the capacity of the membranes for phosphoric acid uptake). On the other hand, in previous work involving the polymerization of pre-sulfonated benzimidazole monomers, we found out that a sulfonated polybenzimidazole derivative presented a conductivity up to two order of magnitude higher than its non-sulfonated analogue (both doped with the same amount of acid) [21]. For this reason we do not rule out a contribution of the sulfonate groups themselves in the present increase of conductivity.

The case for the hybrid ABPBI-PMO₁₂ membrane is very similar. Its conductivity is also higher than that of the ABPBI membrane treated under the same conditions. And, as for the sulfonated derivative, both a larger uptake of acid and the contribution to conductivity of the inorganic acid clusters could be at work in increasing this performance, although the relative importance of each of these factors has not been determined and will be analyzed in future work.

The average activation energy (E_a) for each membrane have been calculated from the slope of the Arrhenius plot, Ln(σ) vs 1000/T (K) and are given in Table 2. In the case of PBI and ABPBI they present similar values. That is in good agreement with our previous observation [11] that for these polymers the E_a decreases when the phosphoric acid content in percentage increases. Furthermore, this also agrees well with the present results, where the sulfonated SABPBI membrane presents the lowest value by far of E_a , associated with an enhanced acid uptake and highest conductivity, with the hybrid ABPBI-PMO₁₂ membrane falling in between the sulfonated derivative and the pristine membranes.

8. Conclusions

We have prepared ABPBI and PBI membranes, and successfully sulfonated previously cast ABPBI

membranes by doping them with sulfuric acid and heat treating the doped membranes at 450 °C in air.

These sulfonated SABPBI membranes have shown an enhanced capacity for phosphoric acid uptake and a consequent increase in conductivity, compared with the non-sulfonated counterparts. The maximum conductivity measured in dry conditions was $3.5 \times 10^{-2} \text{ S cm}^{-2}$ at 185 °C for SABPBI · 4.6 H₃PO₄ with a degree of sulfonation of 41%. These membranes present the same high thermal stability as phosphoric acid doped ABPBI and PBI membranes, which make them interesting for use as membrane in PEMFC at temperatures as high as 150–200 °C.

We have found that not only the sulfonate anions lead to enhanced conductivities for polybenzimidazole membranes. ABPBI–PMO₁₂ hybrid membranes (with inorganic heteropolyacids trapped within the organic polymer network), cast and impregnated with phosphoric acid in the same conditions, also present the same thermal stability and a higher proton conductivity as the benzimidazole membranes described earlier (proton conductivities of ABPBI–PMO₁₂ membranes have reached values of $3.0 \times 10^{-2} \text{ S cm}^{-1}$ at 185 °C).

Thus, both the sulfonate groups and the PMO₁₂ anionic clusters are additives that increase the phosphoric acid uptake. This is important not only to increase the conductivity, but also in order to avoid the leaching of the acid when the membranes operate as fuel cell electrolyte in PEMFC for long times. For the reasons exposed, we consider that the two new membranes reported here are very promising candidates for PEMFC electrolytes at temperatures of at least 185 °C and surely higher.

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