Porous Polybenzimidazole Membranes Doped with Phosphoric Acid: Highly Proton-Conducting Solid Electrolytes

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New proton-conducting polymer electrolytes based on new porous films of polybenzimidazole doped with phosphoric acid have been obtained. The porous polybenzimidazole films were prepared by leaching out a low-molecular-weight compound using a selective solvent of the porogen from polymer/porogen mixtures. This method allows control over the porosity level up to porosities of 75%. The pore size and morphology strongly depend on the porogen/PBI ratio as observed by SEM. The pore size varies from <100 nm with spherical shape for low porosities to very irregular and interconnected structures of 10−15 μm at the highest porosity levels. Different porogens lead to smaller pore sizes in the order dibutyl phthalate>dimethyl phthalate>diphenyl phthalate>triphenyl phosphate. The acid uptake of the membranes, and therefore the ionic conductivity of the films, increases with the porosity. Ionic conductivity as high as 5×10^{-2} S/cm and mechanically stable membranes are easily obtained by soaking the highly porous films in phosphoric acid solutions.

Introduction

Proton exchange membrane fuel cells (PEMFCs) have received a great deal of attention due to their promising application as clean and efficient energy systems. The requirements for the electrolytic polymeric membranes are a good chemical and electrochemical stability, mechanical strength, low permeability to reactant species, high electrolyte transport, high proton ionic conductivity, and low price.[1] Up to now, perfluorosulfonic membranes such as Nafion (Du Pont) and the Dow (Dow Chemical) membrane are the most widely used in both fuel cell research and industry. However, their high cost, low performance at temperatures higher than 100 °C, and high permeability to methanol keep these membranes from application in the direct methanol fuel cell (DMFC), which is recognized as one of the most promising alternative power sources for the transportation sector.

Alternatively, several nonfluorinated membranes have been studied as documented in different reviews.[2] The main approach followed by several groups involves the preparation of high-temperature polymers such as polyamides, polysulfones, or polyimides with pending sulfonic or phosphoric groups. Alternatively, Savinell et al. proposed the direct doping of polybenzimidazole (PBI) by phosphoric acid (H_3PO_4) as solid polymer electrolyte for the methanol fuel cell.[3] The doping of PBI with H_3PO_4 forms a single phase membrane electrolyte, comprising the acid dissolved in the polymer. These membranes exhibited rather high proton conductivity of the order of 5×10^{-3} S/cm at room temperature and up to 4×10^{-2} S/cm at 190 °C. The PBI/H_3PO_4 membranes proved to be resistant to methanol crossover and maintain mechanical strength and toughness in the range of temperatures 20−200 °C. More recently, Savadogo et al. and Bjerrum et al. have increased the ionic conductivity of PBI-based membranes by doping the polymer with other inorganic acids such as H_2SO_4,[4] organic acids,[5] or alkaline bases.[6] As an example, room-temperature conductivity values of 5×10^{-2} S/cm and 9×10^{-2} S/cm were obtained in the case of H_2SO_4-doped PBI and KOH-doped PBI, respectively.

We report here a different concept which employs the introduction of porosity into the PBI as a way to increase the ionic conductivity of the membranes. In this paper we present the micro-structural, thermal, and electrical characterization of new PBI porous membranes doped with H_3PO_4.

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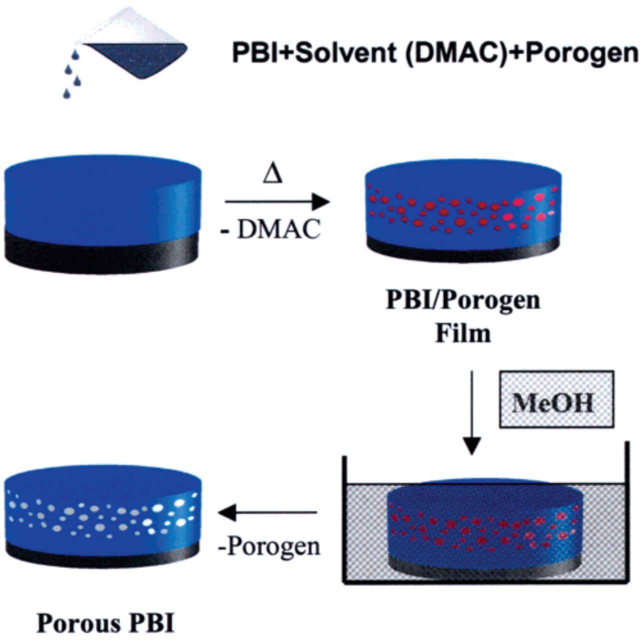
Scheme 1



Experimental Section

Materials. Polybenzimidazole solutions, 26 wt % in dimethyl acetamide, were purchased from Celanese Acetate. All other chemicals were obtained from Aldrich Co. and used as received.

Preparation of Porous Polybenzimidazole Membranes. First, solutions containing PBI and the porogen were cast onto glass plates at room temperature by using a doctor-blade method. Plastisized PBI films were obtained by drying the films at 110 °C for 2 h. Then, the porogen-plastisizer was extracted by immersing the membranes in methanol for 1 h. Finally, the porous PBI was dried at 50 °C until constant weight was acheived.

Doping of PBI Membranes. The porous PBI membranes were doped with H_3PO_4 by immersion in 11 M acid solutions for 4 days and then dried with blotting paper as reported before.[4]

Conductivity Measurements. Ionic conductivity was determined using the complex impedance method at room temperature in a closed cell. The samples were sandwiched between stainless steel blocking electrodes. The impedance measurements were carried out on a computer-interfaced VoltaLab 40 PGZ301 impedance analyzer over the frequency range from 100 kHz to 1 Hz with an AC size wave amplitude of 5 mV. For the "dry" measurements, the membranes were dried at 120 °C for 5 h and the measurements were carried out under dry nitrogen atmosphere.

Morphology of the Membranes. The morphology of the porous membranes was studied by scanning electron microscopy using a JEOL 5500LV scanning electron microscope (SEM). Density measurements were carried out using a flotation weight loss method in a 4-decimals-precision Gram Precision balance.

Results and Discussion

Preparation of Porous PBI Films. Porous PBI membranes were prepared by leaching out a porogen or small-molecular-weight compound from PBI/porogen films. By this method, illustrated in Scheme 1, plastisizer-type compounds such as phthalates or phosphates are used to template porosity into PBI films. In a first stage, PBI/porogen films were prepared by casting PBI/porogen mixtures. During the film formation, once the solvent is evaporated, phase separation occurs, leading to a PBI–porogen blend. In the second stage, the porogen is leached out from the films by immersion in methanol (a selective solvent for the porogens) leading to a porous film. Thus, the morphology of the porous films is related to the structure of the initial PBI–porogen blend composition.

Table 1. Synthesis of Porous PBI

entry	porogen type[a]	initial porogen wt %[b]	% weight loss[c]	density g/cm^3	film aspect
1a	DMP	25	15	1.33	transparent
1b	DMP	50	42	1.01	hazy
1c	DMP	75	72	<0.672	opaque
1d	DEP	25	23	1.34	transparent
1e	DEP	50	49	0.98	hazy
1f	DEP	75	74	<0.672	opaque
1g	DBP	25	25	1.12	transparent
1h	DBP	50	49	0.84	hazy
1i	DBP	75	72	<0.672	opaque
1j	DPP	25	24	1.34	transparent
1k	DPP	50	48	1.10	hazy
1l	DPP	75	73	<0.672	opaque
1m	TPP	25	24	1.30	transparent
1n	TPP	50	48	1.21	hazy
1o	TPP	75	71	<0.672	opaque

[a] Where DMP= dimethyl phthalate, DEP= diethyl phthalate, DBP= dibutyl phthalate, DPP= diphenyl phthalate, and TPF= triphenyl phosphate. [b] Calculated as $W_{dbp}/(W_{dbp} + W_{pbi})$, where W_{dbp} and W_{pbi} are the weights of porogen and polybenzimidazole, respectively, in the membrane. [c] % Weight loss after extraction of the porogen by immersing the membranes in methanol for 4 h.

In this work, we have surveyed different phthalates such as dimethyl, diethyl, dibutyl, and diphenyl, as well as triphenyl phosphate as porogens. First, the use of different solvents and thermal evaporation conditions of the porogen were investigated. For example, in the case of PBI/triphenyl phosphate blends, leaching out the porogen with methanol or toluene, as well as heating the PBI membrane to 200 °C to evaporate the triphenyl phosphate, lead to very similar weight losses after extraction. However, in the case of dibutyl phthalate the best results were obtained when the porogen was extracted with methanol, and consequently we used this method for the rest of our work. Table 1 summarizes the results obtained by varying the PBI/porogen ratio as well as the porogen type. In most cases, after the extraction step, the PBI membranes lose a percentage of weight that correlates with the initial amount of porogen introduced in the film. Furthermore, the thickness of the film stays rather constant and the density drops after the extraction step indicating the generation of a porous membrane and corroborating the validity of our synthetic approach. Among the different porogens, there are not significant differences at the macroscopic level. With the exception of dioctyl phthalate which leads to bad-quality films, the rest of the porogens generate transparent films at porogen ratios <25 wt %, hazy films at porogen ratios of 50 wt %, and opaque films at higher porogen contents. However, the density drop is higher when aliphatic phthalates are used instead of the all aromatic diphenyl phthalate and triphenyl phosphate. In all the cases the porous films were mechanically stable and slightly flexible.

Morphology of the Porous PBI. Scanning electron microscopy (SEM) was employed to study the morphology of the porous membranes. First, we studied the

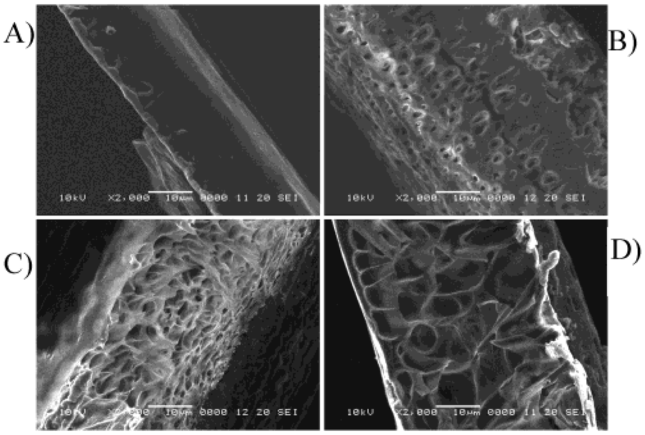


Figure 1. SEM micrographs of cryogenic fractures of porous PBI membranes prepared from PBI/dibutyl phthalate films containing (a) 25 wt % DBP, (b) 50 wt % DBP, (c) 70 wt % DBP, and (d) 80 wt % DBP.

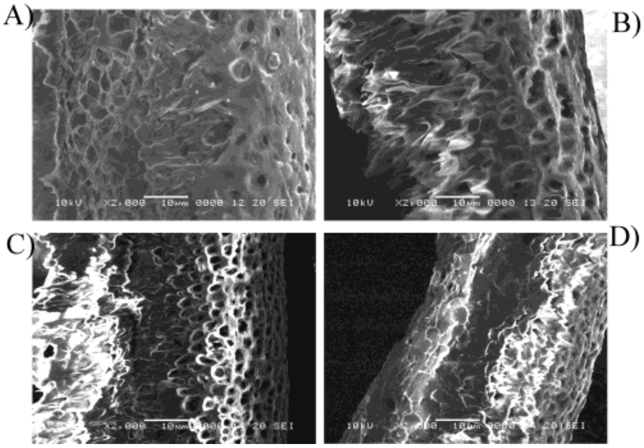


Figure 2. SEM micrographs of cryogenic fractures of porous PBI membranes prepared from 25:75 wt % PBI/porogen films based on (a) dibutyl phthalate, (b) dimethyl phthalate, (c) diphenyl phthalate, and (d) triphenyl phosphate.

effect of the porosity on the morphology of the films. Figure 1a, b, c, and d show the cross-section fractures of PBI porous films generated with dibutyl phthalate in 25, 50, 70, and 80 wt % content, respectively. It is clearly observed how the pore size and porosity increase with the porogen content. At the lowest porogen level, no pores were observed under this magnification. This fact is in agreement with the transparency of the film which indicates that the pores are smaller than 100 nm. The second membrane shows isolated spherical pores with an irregular shape of 1−5 μm. At porogen levels of 70 wt %, the pores are interconnected with an irregular shape of 2−10 μm. Finally, at 80 wt %, the pores are irregular and interconnected structures with a size between 5 and 15 μm. On the other hand, Figure 2 shows the cross-section fractures of porous PBI obtained using 75 wt % of four different porogens: dibutyl phthalate (a); dimethyl phthalate (b); diphenyl phthalate (c); and triphenyl phosphate (d). The porogens containing aliphatic tails, dibutyl and dimethyl phthalate, show a more interconnected and bigger pore size than the “all aromatic” porogens, diphenyl phthalate and triphenyl phosphate, which show smaller and less interconnected pores.

Scheme 2

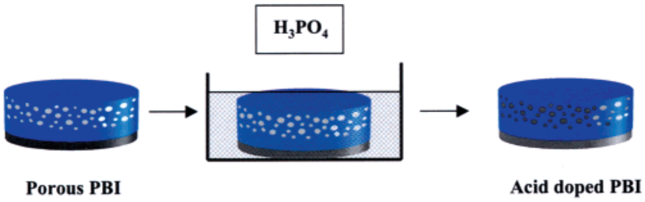


Table 2. Doping with H_3PO_4 (11 M) of Porous Polybenzimidazole Membranes as Prepared Using Dibutyl Phthalate as a Porogen

entry	initial porogen wt %[a]	% weight loss[b]	mass density (g/cm^3)	thickness undoped (μm)	thickness doped (μm)	uptake[c] %
2a	0	0	1.34	46	58	132
2b	15	13	1.30	53	67	156
2c	25	25	1.12	34	38	173
2d	40	40	1.05	60	76	202
2e	50	49	0.84	65	86	246
2f	60	58	<0.67	70	92	396
2g	70	70	<0.67	96	125	439

[a] Calculated as $W_{dbp}/(W_{dbp} + W_{pbi})$, where W_{dbp} and W_{pbi} are the weights of dibutyl phthalate and polybenzimidazole, respectively, in the membrane. [b] % Weight loss after extraction of the dibutyl phthalate by inmersing the membranes in methanol for 1 hour. [c] Calculated as $(W_w - W_d)/W_d$ where W_w and W_d are the weights of the wet and dry membrane, respectively.

Doping of Porous PBI with H_3PO_4 and Conductivity of the Membranes. The concept of doping porous membranes with electrolytic solutions is not new. Actually, Godz and Tarascon et al. successfully applied this idea to the lithium battery using porous poly(vinylidene fluoride-*co*-hexafluoropropylene) membranes.[7] A general observation is that porosity increase is parallel to electrolytic solution uptake which involves a positive increase in ionic conductivity. This method also needs a good affinity between the porous polymer and the electrolytic solution which means that the final result is a gel or plastified polymer. Although several groups have used this strategy for the lithium salt conducting electrolytes[8] there are few examples for proton-conducting materials. In a pioneering work, porous polyoxadiazoles doped with posphoric acid have been reported and proposed as useful membranes for the PEMFC.[9] Similarly, our porous PBI membranes were doped with phosphoric acid by immersion in 11 M H_3PO_4 solutions for 4 days (Scheme 2). The superficial acid excess was finally dried with blotting paper. Table 2 shows the results obtained after doping porous membranes with different levels of porosity. It can be seen that the acid uptake increases from the value of 132% for pure PBI (150% reported in the literature) up to 439% for a porous membrane originated from an initial composition containing 70% dibutyl phthalate. Some authors use the term “acid doping level” which is defined as the molar percent of the acid per repeat unit of PBI. In our case we have calculated a value of 440 mol % for a dense PBI membrane (typical literature

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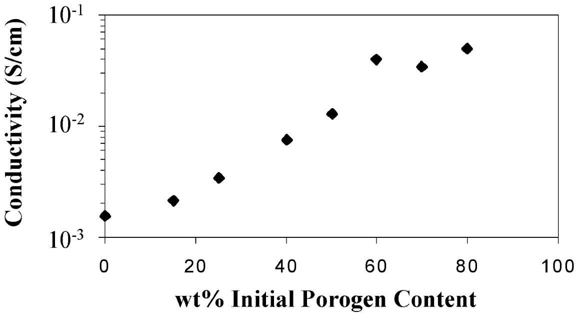

Figure 3. Room-temperature ionic conductivity of different porous PBI samples as a function of the porosity or initial porogen content.

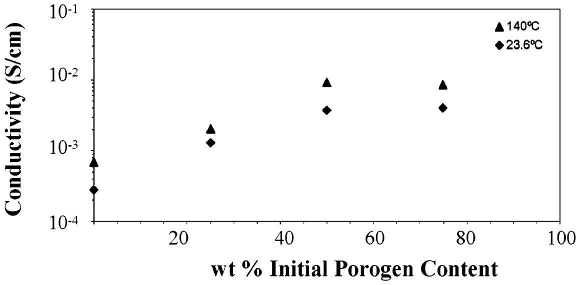

Figure 4. Ionic conductivity of different porous PBI samples after extensive drying of the membranes. Measurements were performed at 0% relative humidity at room temperature and 140 °C, respectively.

values are 450−500 mol %) and this value increases to 1460 mol % in the case of the 70% porous membrane. The room-temperature ionic conductivity of these membranes was determined by impedance spectroscopy. In parallel to the increase in acid uptake, the ionic conductivity of doped membranes increases linearly with the initial porosity of the films. This effect is illustrated in Figure 3 which shows the ionic conductivity versus the initial porogen content. The conductivity increases from 1.5×10^{-3} S/cm obtained for the bulk polymer to a maximum value of 5×10^{-2} S/cm measured for a doped porous membrane with an initial porogen content of 70 wt %. Furthermore, the membranes show a very small decrease in conductivity (<10%) after one year of storage. It seems obvious that concentrated H_3PO_4 adsorbs better inside the porous film, leading to a higher acid uptake and therefore to a higher conductivity. It is worth noting that the conductivities obtained in this work with doped porous polybenzimidizale are similar to those reported for Nafion at room temperature.[10] The dependence of the conductivity on the porogen content at both 23.6 and 140 °C is shown in Figure 4. In these cases the ionic conductivity was measured after drying the membranes at 120 °C for 5 h and under equilibrated dry nitrogen atmosphere. Because of this, the room-temperature values are lower than those shown before. Interestingly, the conductivity is found to increase with the porogen content. Furthermore, ionic conductivity at 140 °C shows very high values in contrast to that observed with Nafion membranes where conductivity drops at temperatures higher than 100 °C due to the crucial influence of water in the conductivity. Further work is in progress to determine whether the porous structure and the conductivity will be stable enough over a long period of time under the working conditions of a fuel cell and whether the permeability of the membranes to reactants such as methanol is low enough to allow high-efficiency fuel cell operation.

Conclusions

Using a novel approach, new porous PBI films were prepared by leaching out a low-molecular-weight compound using a selective solvent of the porogen from polymer/porogen mixtures. This method allows control over the porosity level up to porosities of 75%. The morphology of the porous films strongly depends on the porogen/PBI ratio and the chemical nature of the porogen. The pore size and microstructure varies from <100 nm with spherical shape for low porosities to very irregular and interconnected structures of 2−15 μm at the highest porosities. High room-temperature proton conductivities are easily obtained by soaking the films in concentrated H_3PO_4.

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