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Influence of composition and acid treatment on proton conduction of composite polybenzimidazole membranes

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Abstract

Inorganic/organic composite membranes formed by polybenzimidazole, silicotungstic acid and silica with different ratio between them have been prepared and characterized before and after treatment in phosphoric acid in order to evaluate the influence of composition and acid treatment on some main characteristics of the membranes. In particular the proton conductivity, the mechanical stability and the structural characteristics of the membranes were evaluated. Silica behaved as a support on which the heteropolyacid remained blocked in finely dispersed state and as an adsorbent for water, thus determining a beneficial effect on proton conduction. The membrane with 50 wt.% of SiWA–SiO_2/PBI, mechanically stable, gave proton conductivity of 1.2×10^{-3} S cm^{-1} at 160°C and 100% relative humidity. After treatment with phosphoric acid the proton conductivity of membranes increased to 2.23×10^{-3} S cm^{-1} under the same test conditions. All the materials prepared had amorphous structure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Solid electrolyte; Conductive membrane; Proton conduction; Silicotungstic acid; Polybenzimidazole

1. Introduction

The crystalline forms of phospotungstic and phosphomolibdic acid (two compounds of the family of heteropolyacids) containing maximal number of water molecules in their reticular structures exhibit very high proton conductivity [1]. However, they are very sensitive to surrounding conditions: relative humidity and temperature [2,3] which can modify the crystalline structure of these heteropolyacids or transform them into the solution. Thus, it is difficult to manage these materials as solid electrolytes with stable crystalline structure in technological devices, like fuel cells, where water is produced during operation. Concentrating the attention on the more studied among the two heteropolyacids, the phosphotungstic acid, it is known thats this material exists in different crystalline structures each having a different number of water molecules. The crystalline structure with 29 water molecules gives the highest proton conductivity and only this would be suitable as a solid electrolyte for fuel cell applications. Another possibility for the application in this field would be the utilization of heteropolyacid as the concentrated solution, because it has very high proton conductivity [4]. In fact, recent results of experiments with fuel cell working with the phosphotungstic acid in solid or concentrated solution form demonstrate very interesting electrochemical performance [4,5]. Power density of about 700 mW cm^{-2} was drawn from a laboratory scale H_2/O_2 fuel cell operating at room temperature and at 1 atm pressure of the gases. Unfortunately, during the cell operation, the solid electrolyte dissolved in the electrochemically-produced water and it leaked out through the gas outlet tubes. The dissolved electrolyte flooded the electrodes, thus creating gas diffusion problems. Electrolyte dissolution and electrode flooding had detrimental effects for the proper operation of the fuel cell. During the fuel cell tests we also observed that the heteropolyacid electrolyte had a protective effect against the CO poisoning of platinum catalyst present in the anode [6]. Because the CO is a gas always present in hydrogen obtained by reforming processes of common fuels and because the commonly utilized purification processes do not eliminate it completely from the gas stream, the methods by which one can prevent the catalyst from being poisoned during the fuel cell operation are of extreme interest. The heteropolyacid exhibited also a promoting effect on the electrochemical reduction of oxygen at the fuel cell cathode [7]. These interesting aspects of the phosphotungstic acid electrolyte justified the orientation of research activity towards the fixation of the heteropolyacids in stable structures so that they could become water-insoluble while

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retaining their high proton conductivity. Mioc et al. entrapped the phosphotungstic acid on silica and aluminosilicate [8,9] and we entrapped the phosphotungstic and silicotungstic acid on silica [10]. But these composite materials, although stable in the presence of water, cannot be used as electrolytes in fuel cells, because they are in powder form. For this reason we have tried to develop a composite membrane using a polymer as binder for the formation of mechanically resistant membranes with low gas permeability. The silicotungstic acid on silica was chosen as the inorganic proton conductor material and the polybenzimidazole as the binding polymer. Silicotungstic acid was preferred over phosphotungstic acid because it forms more stable materials when adsorbed on silica and in similar conditions displays higher proton conductivity [10]. The polybenzimidazole was chosen for its characteristic to form mechanical and thermal resistant layer [11]. The polymeric material is normally a good electric insulator but properly treated with phosphoric acid or with sulfonic acid group donors it becomes a proton conductor material as evidenced in recent papers by Wainright et al. [12] and Glipa et al. [13].

In this paper, the preparation procedure of membranes containing different amounts of silicotungstic acid, silica and polybenzimidazole will be reported together with the proton conductivity, mechanical and structural characteristics. Both, the effects of silica and phosphoric acid treatment on proton conductivity of membranes will be presented and an optimal composition of membrane will be given.

2. Experimental

2.1. Preparation of the membranes

The powders containing 23, 37.9, 45 and 60 wt.% of silicotungstic acid on silica was used for the preparation of composite membranes. Three composite membranes with different amounts of inorganic material in polybenzimidazole were prepared starting from the SiWA/SiO$_2$ powder with 45 wt.% SiWA in it. Two composite membranes were prepared starting from SiWA/SiO$_2$ powder with 60 wt.% of SiWA in it. The next two composite membranes were prepared starting from SiWA/SiO$_2$ powders: one with the 23 wt.% and another with the 37.9 wt.% of SiWA in the powder. In such a way we could compare membranes in which the amounts of inorganic material and polymer varied reciprocally while the amount of SiWA on SiO$_2$ remained constant. A sample formed of 50% of SiWA on polybenzimidazole and without silica was prepared as the reference. The designations of prepared membranes, their composition, thickness and properties are listed in Table 1. The composition of membranes is given also in Fig. 1 as the ternary system diagram. The silicotungstic acid was a fluka product and the silica was fumed silica Cab-o-sil EH-5 (surface area: 380 ± 30 m^2 g^{-1}) produced by Cabot. The preparation procedure consisted in the dissolution of the silicotungstic acid in water with the subsequent introduction of the so prepared solution into the stirred silica suspension. The obtained mixture was dried at 60–70°C and then ground in a ball mill. The powder was dispersed in a little amount of water and neutralized by addition of a 1N NaOH solution. Then the suspension was evaporated and the remaining powder was ground again. The neutralization of the supported silicotungstic acid was a necessary step to avoid the precipitation of the polybenzimidazole when the inorganic material was

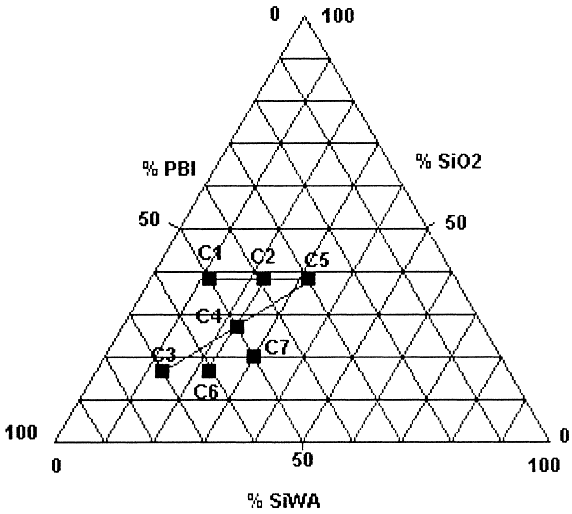

Fig. 1. Graphical representation of membrane compositions.

Table 1
List of the composite membranes with compositions and the mechanical and wettability properties

Sample	SiWA/SiO$_2$ (%)	SiWA (%)	SiO$_2$ (%)	PBI (%)	Thickness (μm)	Mechanical stability	Wettability
C0	0	50	0	50	80	Stable	Non-wettable
C1	23	11.5	38.5	50	95	Stable	Wettable
C2	37.9	22.5	38.5	39	95	Stable	Wettable
C3	45	13.5	16.5	70	80	Stable	Wettable
C4	45	22.5	27.5	50	90	Stable	Wettable
C5	45	31.5	38.5	30	100	Brittle	Wettable
C6	60	22.5	15	62.5	80	Stable	Wettable
C7	60	30	20	50	95	Stable	Wettable

added to the polymer solution. The polybenzimidazole (PBI) in powder form was purchased from Aldrich. To obtain the solution for the preparation of membranes it was dissolved in *N,N*-dimethylacetamide at 150°C for 15 h. The solution was subsequently filtered to eliminate any polymer particles from the suspension. For each membrane, the proper quantity of inorganic material and polybenzimidazole solution was thoroughly mixed in an agate mortar to form a homogeneous paste, which was then spread at constant thickness on a flat glass surface. After the evaporation of solvent at 60–70°C for 5–6 h, the membrane formed on the glass surface. The so obtained membranes, with thickness 80–100 μm, were first rinsed with distilled water and then immersed into a 4N HCl solution for 24 h. Finally, they were boiled for 1 h in distilled water. The treatment of membranes with the acid solution was carried out in order to reintroduce the protons instead of sodium ions. The membranes were divided in two parts and one part of each membrane was immersed in 50 wt.% phosphoric acid solution at room temperature for 24 h. The acid treated membranes were rinsed with water and then held in boiling distilled water for 2 h. Both the phosphoric acid-treated and non-treated membranes were held in distilled water until the beginning of characterization tests.

2.2. Proton conductivity measurements

Proton conductivity measurements were made placing a 1 cm^2 disc of each membrane between two gold discs and mounted in a closed conductivity measurement cell. A little amount of water in the cell maintained the relative humidity at 100%. The cell was connected to universal bridge working at the frequency of 1 kHz. The measurements were performed at various temperatures in the range from 40 to 160°C on the membranes treated and non-treated with phosphoric acid. The results, obtained in the form of resistance, have been uniformed for the geometric surface and the thickness and reported as specific conductivities.

2.3. Mechanical resistance tests

Mechanical resistance to bending stress was qualitatively determined for the prepared membranes by an apparatus made "in house". It consisted of a vertical metallic bar, which finished at the lower part with a sphere of diameter 0.3 cm. The bar was free to move in the vertical direction and a weight of 100 g was placed over the bar. For the test the sphere was carefully put on the strip of the membrane sample, which was 1 cm width and was fixed on two opposite sides at the distance of 1 cm. The space under the sample was empty so that exclusively the membrane sustained the pressure exerted by the sphere (loaded with 100 g). Through this apparatus it was possible qualitatively to discriminate the mechanical resistant membranes, which do not crack under the pressure of the sphere, from the brittle ones.

2.4. X-ray diffraction analyses

X-ray diffractograms were scanned on the silica and the different SiWA/SiO$_2$ powders and on pure PBI membrane and composite membranes containing SiWA, SiO$_2$ and PBI. Analyses were carried out with a Philips X-Pert diffractometer using a Cu Kα radiation and operating at 40 kV and 30 mA. The diffractometer consisted of a PW 1830 HT-generator and a PW 3710 control unit which was controlled by a PC computer equipped with a Philips PC-APD software. Continuos scans were collected by using a Bragg–Brentano para-focusing optical system. The X-ray diffraction patterns were collected with a scan rate of 0.5° min^{-1}.

3. Results and discussion

The results of proton conductivity measurements obtained for the different membranes at the condition of 100% relative humidity and in the range of temperature from 40 to 160°C are reported in Fig. 2. An increase of conductivity was observed for all the samples by increasing the temperature. Two of the membranes prepared with the 45% SiWA/SiO$_2$ (samples C4, C5) showed the highest conductivity with respect to all the others and between them the conductivity was higher for the sample C5 which had the higher amounts of inorganic components (silica and SiWA). A maximum value of 3.12×10^{-3} S cm^{-1} was obtained at 160°C with the membrane containing 70% of inorganic component. Unfortunately this membrane was not mechanically stable when subjected to the bending test. On the contrary, the membrane with 50% of inorganic material was mechanically stable, but its proton conductivity was lower at the same conditions, i.e. 1.2×10^{-3} S cm^{-1}. In any case the conductivity of this membrane was about 5 orders of magnitude higher than that of the membrane prepared with 50% of pure silicotungstic acid in polybenzimidazole, the conductivity of which was under similar conditions about 10^{-8} S cm^{-1}. Thus, the silica improved the conductivity characteristics of the membranes probably increasing water absorption and creating an easier path for proton motion. Simple wettability tests showed that the membrane composed of pure SiWA and PBI was hydrophobic while the membranes composed of SiWA, SiO$_2$ and PBI behaved as hydrophilic materials. Table 1 also report the mechanical and wettability characteristics of the membranes. To discriminate between the effects of silica and SiWA on proton conductivity the samples C1 and C7 were prepared and tested. With respect to the C4, the C1 and C7 samples gave lower proton conductivity. It is probable that the SiWA loading (11.5%) in sample C1 is too low to sustain an electrolyte continuity inside the membrane and the SiO$_2$ loading (20%) in sample C7 is insufficient to keep enough water to sustain proton motion despite the relatively high acid content (30%). Comparing the samples C1, C2 and C5 evidences the

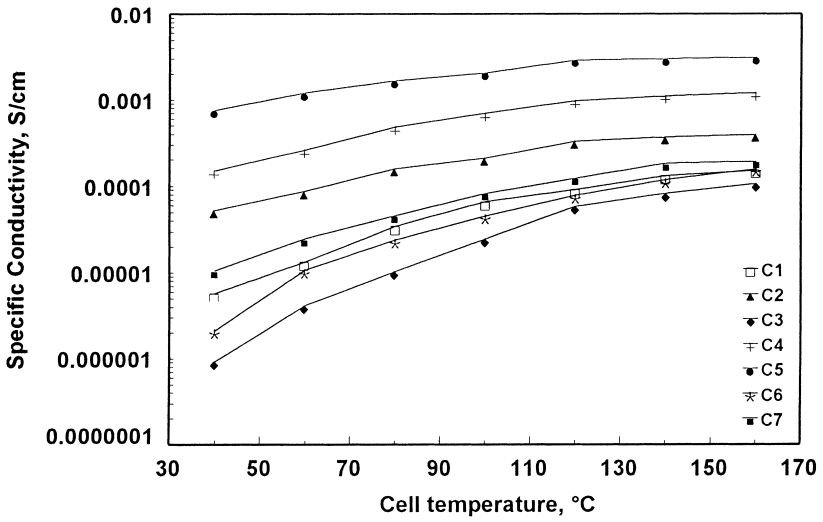

Fig. 2. Proton conductivity of composite membranes with different composition as a function of temperature. Relative humidity: 100%.

variation of proton conductivity of membrane at fixed amount of silica. The proton conductivity increased by increasing the SiWA loading. The membranes C2, C4 and C6 have the same SiWA and different SiO_2 and PBI loading. The proton conductivity of C6 sample is lower than that of the other two samples. The sample C2 is less conductive than C4 sample. Proton conduction in C6 sample is obviously limited by the low amount of silica which does not maintain enough water in the membrane, while in the C2 sample probably a too high dispersion of acid on the silica breaks the acid continuity in the membrane. The proton conductivity of these membranes was too low for their application in fuel cell systems. To enhance this characteristic the samples were treated additionally in phosphoric acid solution. The proton conductivity of representative samples of membranes, C2, C4 and C5, treated with phosphoric acid and designated as C2P, C4P and C5P are reported in Fig. 3. In all cases the treatment with phosphoric acid increases the proton conductivity of the membranes. A value of 5.2×10^{-3} S cm^{-1} was recorded for the C5P sample at 160°C and 100% relative humidity. As we already discussed, this membrane is not applicable, because it is brittle. Instead, it is more interesting to notice that the proton conductivity of the mechanically stable membrane, C4P, gave a value of 2.23×10^{-3} S cm^{-1} under the same operation conditions reported above.

The XRD patterns of three representative membranes are reported together with XRD patterns of PBI and 45% SiWA/SiO_2 in Fig. 4. No diffraction peaks, characteristic for SiWA appear in the spectrum of material containing 45% of SiWA/SiO_2. This is a consequence of finely dispersed HPAs on the surface of silica and the sample behaves as X-ray amorphous. The X-ray diffraction patterns of the membranes present very broad peaks in the region of 2Θ from 15 to 35, which denotes that the materials are mainly amorphous. The

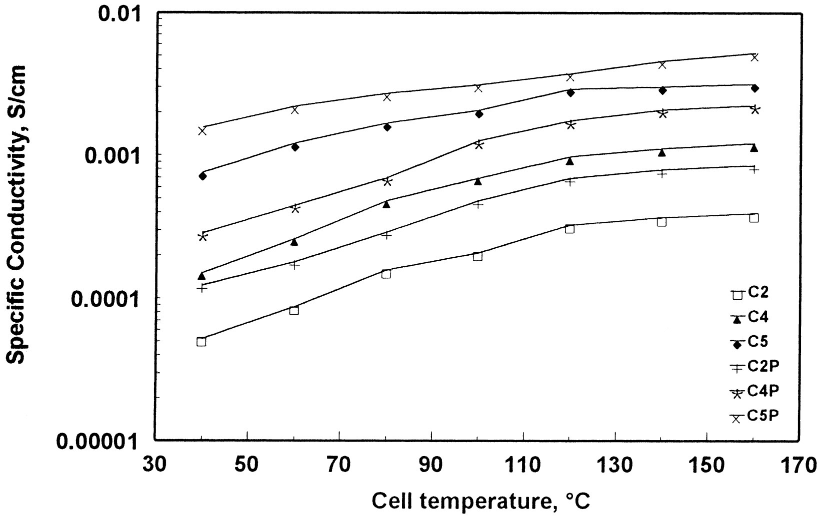

Fig. 3. Proton conduction of representative composite membranes non-treated and treated in phosphoric acid as a function of temperature. Relative humidity: 100%.

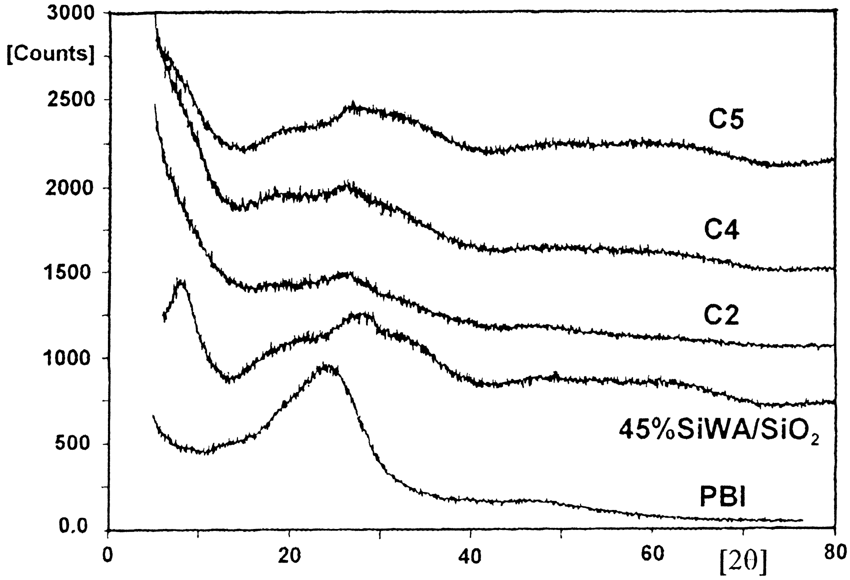

Fig. 4. X-ray diffraction patterns of samples of PBI, 45% SiWA/SiO$_2$ and composite membranes non-treated in phosphoric acid.

absence of the characteristic peaks of SiWA in the composite membranes denotes that the acid is still uniformly distributed on silica (no agglomeration had occurred) after the preparation process of membranes.

4. Conclusions

Composite membranes with thickness 80–100 μm and with good mechanical properties were prepared by using SiWA and silica as inorganic materials and polybenzimidazole as binding polymer. The treatment of the composite membranes with phosphoric acid enhances their proton conductivity. The silica has the double function of entrapping the heteropolyacid avoiding its dissolution in water, and retaining water thus improving the proton conduction. The as-prepared membrane with 50 wt.% of inorganic material is mechanically stable and gives proton conductivity of 1.2×10^{-3} S cm^{-1} at 160°C and 100% relative humidity. The same membrane, after the phosphoric acid treatment, gives proton conductivity of 2.23×10^{-3} S cm^{-1} under the same test conditions.

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