SULFONATED POLYETHER ETHERKETONE-POLY(PHENYLENEDIAMINE DERIVATES) COMPOSITE MEMBRANES FOR FUEL CELL APPLICATIONS

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This paper presents the synthesis of two sulfonated polyether etherketone composite membranes doped with poly(p-phenylenediamine) in the presence of hydroquinone and poly(o-phenylendiamine) . The support membranes were obtained by the phase inversion process, the conductive polymers were synthesized by in situ polymerization into the membrane pores and they were doped with polystyrene sulfonic acidin order to increase the conductivity

The structure and morphology of the obtained membranes were studied by FT-IR spectroscopy and SEM microscopy, the ionic conductivity were determined by Electrochemical Impedance Spectroscopy and permeation measurements were performed to study the transport through the membranes.

Keywords: composite membranes, sulfonated polyether etherketone, poly(p-phenylenediamine), poly(o-phenylenediamine), hydroquinone, ionic conductivity

1. Introduction

Fuel cells are considered to be a viable eco-friendly technology for energy conversion, mostly because of the near zero emission characteristic, especially in the current context, when the traditional fuels are more expensive and likely to became very rare in the next 50 years [1-3]. In the last 20 years the technology advanced so that fuel cells can be used for providing power in stationary and portable applications and can replace the internal combustion engine [4].

Various proton-conducting polymer electrolyte membranes have been studied for the operating conditions in the fuel cell [3]. Currently the widely used materials for these membranes are perfluorinated polymers, mostly Nafion and its

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derivates, but beside their advantages like good stability and high proton conductivity they present some important draw backs like the fact that they don't provide a good barrier for methanol cross over and have high costs [5, 6]. On the other hand sulfonated polyether etherketone - sPEEK - presents a great interest as a support polymer in proton exchange membranes as it displays good thermal, mechanical and chemical stability, high proton conductivity and low methanol cross over [5, 7].

Conductive polymers are a class of materials which presents interesting properties because they combine the characteristics of organic polymer and the electric properties similar to those of metals [8]. From these polymer, polyaniline - PANi - is one of the most investigated because of its outstanding environmental stability, easy synthesis rout, oxidation or protonation-adjustable electrical properties and its potential use as a component of electrochromic devices, sensors and separation membranes [9, 10]. In the recent years some research have been employed to prepare conjugated polymers, with better chemical functionality, mechanical and thermal properties than PANi, starting from phenylendiamines (ortho, meta, para derivates) [10, 11].

This paper reports the synthesis and characterization of two composite membranes with sPEEK and phenylenediamine derivates conductive polymers to increase the total conductivity of the materials. The two membranes are: sulfonated polyether etherketone-poly(p-phenylenediamine) - sPEEK-PpPD(h) - with the conductive polymer synthesized by in situ polymerization, into the membranes pores, in the presence of hydroquinone and sulfonated polyether etherketone-poly(o-phenylenediamine) - sPEEK-PoPD - also with the conductive polymer synthesized by in situ polymerization. Analyses were conduct to establish the structure and the characteristics of the two composite membranes.

2. Experimental

2.1. Membranes synthesis

For the composite membranes synthesis polyether etherketone, M = 150000 g/mol (Aldrich), sulfuric acid H_2SO_4 96% (Merck), p-phenylenediamine, o-phenylenediamine, hydroquinone, HCl 37%, potassium persulfate $K_2S_2O_8$ (Fluka), polystyrene sulfonic acid (Fluka) and distilled water were used.

The synthesis of the sulfoneted polyether etherketone support membranes by the phase inversion process was carried out as presented in other research paper [12].

The doping process of the support membrane with poly(p-phenylenediamine) was carried out as follows. sPEEK membranes were immersed in water with HCl and sprinkled with a salt of p-phenylenediamine and hydroquinone, then they were let to react in this solution for a couple of hours,

time for p-phenylenediamine and hydroquinone to enter within the pores, process that can be observed from the changing color of membranes from white to yellow. Then, $K_2S_2O_8$ and HCl were added to this solution so that the p-phenylenediamine can polymerize. The polymerization is evidenced by the fact that the color of the membranes begins to turn blue and after several hours, when the reaction stops, it turns to black. Some crystals, possibly of calcium, were formed at the surface of the membrane, but they were dissolved in water, as the obtained membranes are kept in water. The proposed scheme of reaction for the synthesis of sPEEK-PpPD(h) composite membrane is presented in Fig.1.

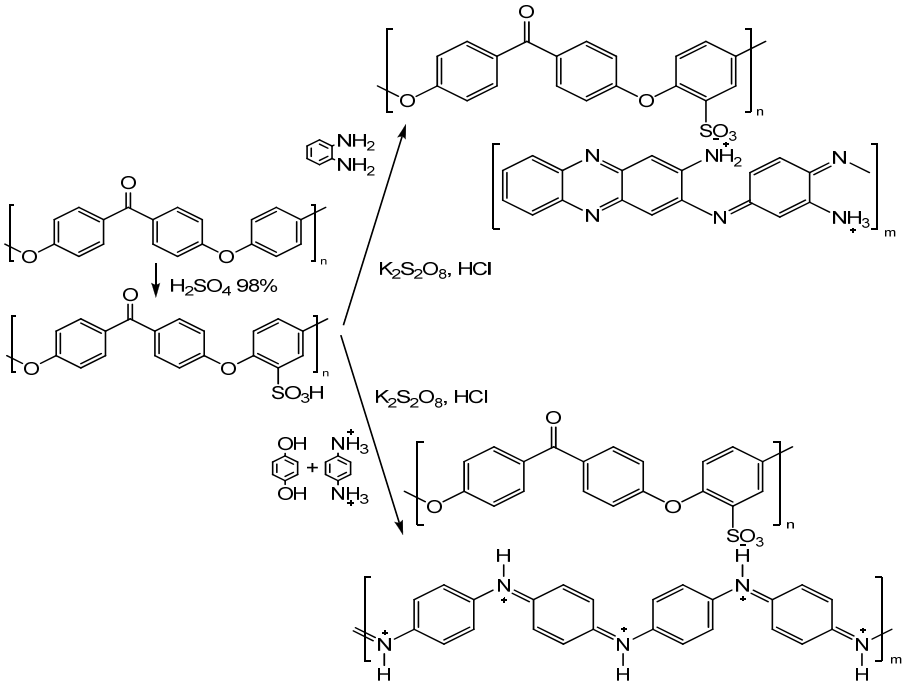

Fig 1. Proposed schematic reaction for the synthesis of the sPEEK-PpPD(h) and sPEEK-PoPD composite membranes.

The doping with poly(o-phenylenediamine) was carried out in a similar manner. Thereby the sPEEK membranes were immersed in water, sprinkled with o-phenylenediamine and let to react. Then $K_2S_2O_8$ and HCl were added so that the polymerization of o-phenylenediamine can take place. The membranes were let in the polymerization solution for several hours, time in which they change their color from yellow to black. After this the membranes were kept in water where some crystals, similar to those from the sPEEK-PpPD(h) membranes, were formed, but these didn't dissolve in water. More than that, after a couple of days

in water the membranes turned from black to dark brown. Also the proposed scheme of reaction can be seen in Fig. 1.

The conductive polymers from the composite membranes were doped with polystyrene sulfonic acid, process that took place by immersing the membranes in a solution of polystyrene sulfonic acid in water.

2.2. Membranes characterization

The *FT-IR spectroscopy* was performed using a Bruker Tensor 27 Instrument with ATR diamond annex. Samples of the sPEEK-PpPD(h) and sPEEK-PoPD composite membranes, simple and doped with polystyrene sulfonic acid, were analyzed, after they were dried out of the water they were kept in.

The *SEM microscopy* was performed with a FEI Instrument in order to gather information about the morphology of the membranes. Thereby samples of the sPEEK-PpPD(h) and sPEEK-PoPD composite membranes were analyzed.

From the *Electrochemical Impedance Spectroscopy* performed on the sPEEK-PpPD(h) and sPEEK-PoPD composite membranes doped with polystyrene sulfonic acid the ionic conductivity - an important characteristic for membranes for fuel cell applications - and the capacitance of the membranes were evaluated. The measurements were conduct - using a VoltaLab 40 Dynamic Electrochemical System - at a temperature of 25°C, with hydrated membranes, using an electrochemical cell consisted of two disk platinum electrodes with a surface of 0.9503 cm^2, placed inside the jaws of a digital precision micrometer provided with mobile reference origin, having as electrolyte the membranes that are analyzed placed between the electrodes [13]. The frequency range scanned was between 100 kHz and 100 mHz using a potential amplitude perturbation of 50 mV. The cell is able to determine the membrane thickness during the measurements and the software of the analytical system has incorporated a circular regression procedure that supplies the values of the ohmic resistance R_1, the polarization resistance R_2 and the double layer capacitance C [13].

The *permeation measurements* were carried out for the sPEEK-PpPD(h) composite membrane using a filter funnel. The time in which 100 mL distilled water passed through the membrane, with the surface area of 0.005 m^2, was measured and the permeation fluxes from 5 to 5 minutes were calculated.

3. Results and discussions

3.1. FT-IR spectroscopy

From the spectra images, presented in Fig. 2, it can be observed that both the undoped and doped composite membranes present similar spectra, some minor differences being detected in the intensity, in terms of absorbance units, and also in the localization of some peaks. Because of this similarity all four spectra are

presented as one, as follows: the specific bands for the PEEK segment are represented by the peak at 1250 cm^{-1} attributed to the etheric bond C-O-C, the peak at 1635 cm^{-1} attributed to the conjugated ketonic bond; the sulfonic groups, characteristic both for sPEEK and for the doped membranes with polystyrene sulfonic acid, are represented by the peak at 1078 cm^{-1} attributed to the O=S=O symmetric stretch, and the peak at 1020 cm^{-1} attributed to the S=O symmetric stretch; the bands characteristic both for sPEEK and the conductive polymers, as they are attributed to the aromatic ring, are represented by the peaks at 1500 and 1590 cm^{-1} attributed to C=C-C aromatic ring stretch; the specific bands for the conductive polymers are represented by the peak at 1285 cm^{-1} attributed to C-N stretching vibration of the aromatic secondary amino group and the peak at 3350 cm^{-1} attributed to the secondary N-H stretch vibration.

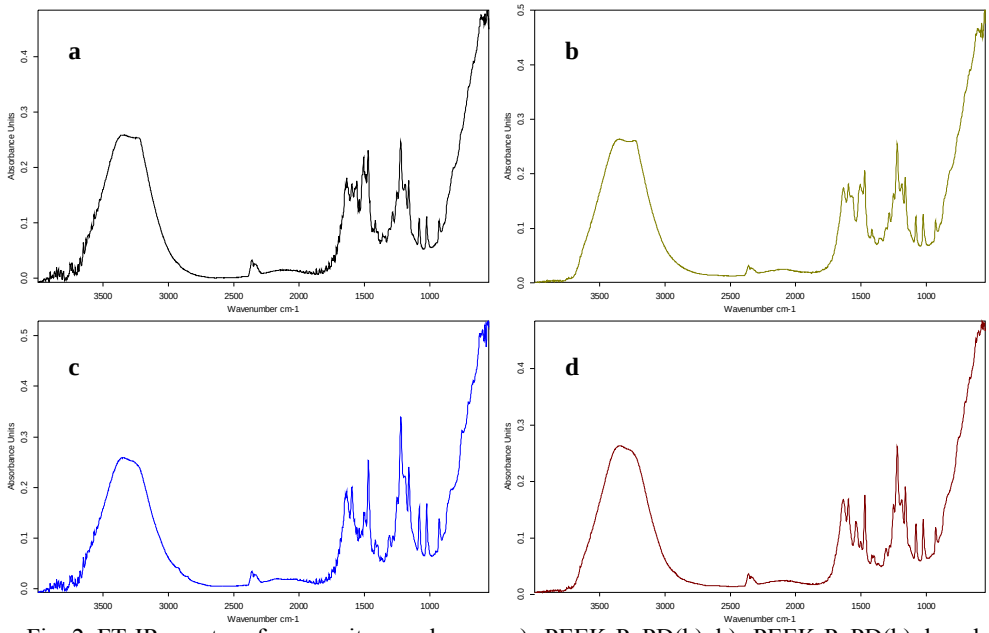

Fig. 2. FT-IR spectra of composite membranes: a) sPEEK-PpPD(h), b) sPEEK-PpPD(h) doped with polystyrene sulfonic acid, c) sPEEK-PoPD, d) sPEEK-PoPD doped with polystyrene sulfonic acid.

3.2. SEM microscopy

Fig. 3 presents the SEM images, surface and section, of the sPEEK membranes, wherefrom the formation of a homogenous material can be observed. The pore size of the membrane varies from 1 to 3 μm at the surface and from 8 to 17 μm in section.

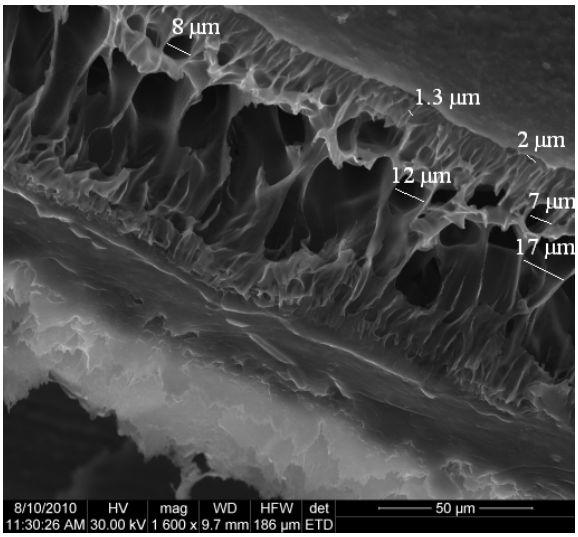

Fig. 3. SEM images of sPEEK membranes -section.

From Fig. 4, the SEM images of the two composite membranes studied, it can be observed a difference towards the sPEEK membrane and also that the tow materials have similar morphologies, the conductive polymers being synthesized at the surface and within the pores of the membranes as conglomerates.

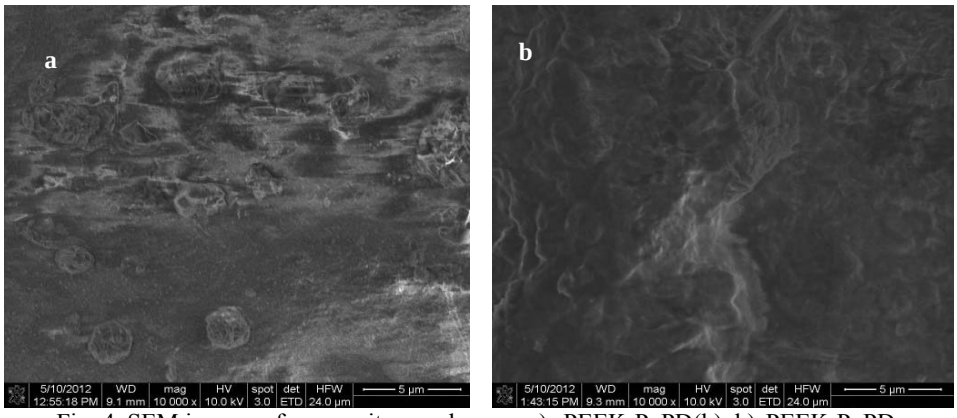

Fig. 4. SEM images of composite membranes: a) sPEEK-PpPD(h), b)sPEEK-PoPD.

3.3. Electrochemical Impedance Spectroscopy

The ionic conductivity (σ) and capacitance (C) for obtained membranes were evaluated by Electrochemical Impedance Spectroscopy. The results were determined from the electrochemical impedance spectra in the form of Nyquist diagrams, presented in Fig. 5.

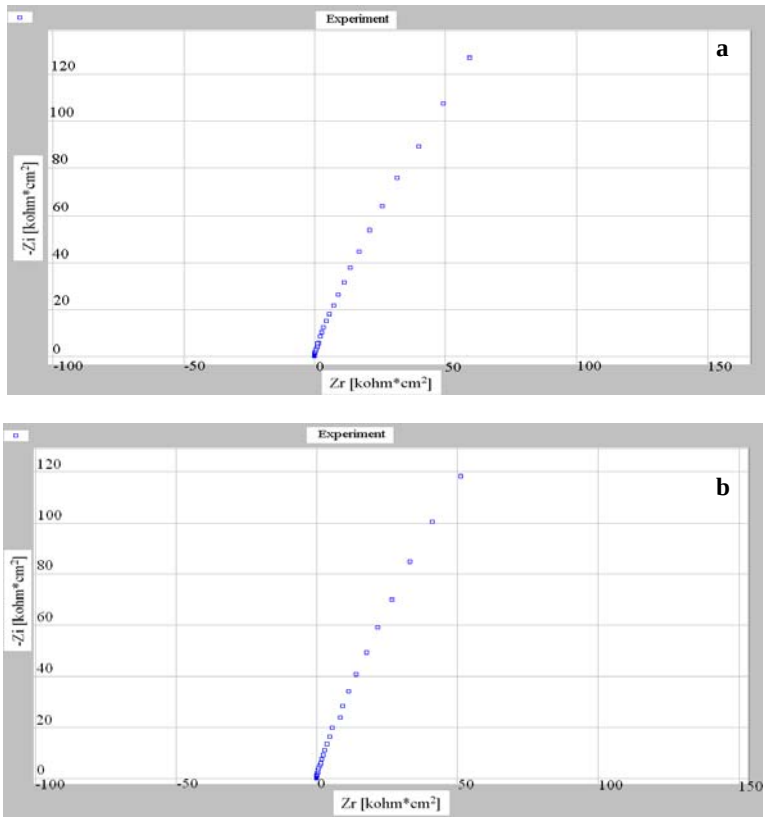

Fig. 5. Nyquist diagrams of: a) sPEEK-PpPD(h) and b) sPEEK-PoPD composite membranes doped with polystyrene sulfonic acid.

The ionic conductivity was calculated with the formula number 1 and the results are presented in table 1.

$$\sigma = \frac{d}{R_1} \tag{1}$$

where:

σ - the ionic conductivity, Scm^{-1};
d - the membrane thickness, cm;
R_1 - the ohmic resistance, Ωcm^2.

Table 1

The ionic conductivity and capacitance of the composite membranes doped with polystyrene sulfonic acid

Membranes	d (cm)	R_1 (Ωcm^2)	C (μFcm^{-2})	σ (Scm^{-1})
sPEEK-PpPD(h)	0.0532	3.833	0.824	0.0139
sPEEK-PoPD	0.0653	12.28	1.124	0.0053

From these results it can be observed that the sPEEK-PpPD(h) composite membrane has a better ionic conductivity, up to 2.5 times higher, than the sPEEK-PoPD composite membranes even if they have a similar structure (but this value is smaller than those reported for Nafion membranes 0.083 - 0.1 Scm^{-1} [14, 15]). This can be due to the hydroquinone presence in the polymerization process since when is not used, the ionic conductivity is in the same size range as that of sPEEK-PoPD membrane (fact studied in another research).

3.4. Permeation measurements

The permeation measurements were performed just for the sPEEK-PpPD(h) composite membrane since it presents the higher ionic conductivity from the two considered membranes and has more chances to be use for fuel cell applications, so the transport through the membrane is an important condition.

Table 2

The permeation flux of distilled water through the sPEEK-PpPD(h) composite membrane

Time (min)	Volume (mL)	Permeation Flux ($Lm^{-2}h^{-1}$)
5	11	26.274
10	24	28.662
15	33	26.274
20	41	24.482
25	48	22.930
30	55	21.895
35	61	20.814
40	67	20.004
45	73	19.374
50	77	18.392
55	81	17.588
60	85	16.919
65	88	16.169
70	90	15.355
75	93	14.809
80	95	14.182
85	96	13.488
88	97	13.164

The permeation fluxes, calculated with formula number 2, are presented in table 2, wherefrom it can be observed that water passes through the membrane in 88 minutes and the permeation flux decreases almost linear from 26.274 $Lm^{-2}h^{-1}$ to 13.164 $Lm^{-2}h^{-1}$. This decrease is due to the shrinking of the membrane pores size as they retain water molecules.

$$PF = \frac{V}{S * t} \tag{2}$$

where:

PF - permeation fluxes, $Lm^{-2}h^{-1}$;

V - the volume of water, L;

S - the surface of the membrane, m^2;

t - the time in which the volume of water pass through the membrane, h.

4. Conclusions

This paper presents the synthesis of two new composite membranes with sulfonated polyether etherketone as support polymer doped by in situ polymerization with conductive polymers like poly(p-phenylenediamine) and poly(o-phenylenediamine).

From the FT-IR spectroscopy and SEM microscopy analyses it can be observed that the two membranes have a similar structure and morphology that can be explained by the similar route of synthesis. The most important characteristic of such membranes with potential applications in fuel cell is the ionic conductivity, which has the values of 0.0139 Scm^{-1} for sPEEK-PpPD(h), and 0.0053 Scm^{-1} for sPEEK-PoPD. The transport through the membranes was studied by means of permeation fluxes.

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