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Characterization and application of composite membranes in DMFC

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Abstract

The present work focuses on the characterization of membranes for direct methanol fuel cells (DMFC), prepared using composites of sulfonated poly(ether ether ketone) (sPEEK, with sulfonation degree, SD, of 42 and 68%) as polymer matrix. This polymer was inorganically modified incorporating different amounts of zirconium phosphate (ZrPh) pretreated with *n*-propylamine and polybenzimidazole (PBI). The investigated properties were: proton conductivity, water and aqueous methanol swelling, permeability coefficients for DMFC species and morphology. DMFC tests were performed at 110 °C with relative humidity (r.h.) in the cathode feed of 100 and 138%. The results obtained show that the inorganic modification of the polymer decreases the proton conductivity, water and aqueous methanol swelling and permeability towards DMFC species. In terms of morphology, it was found that the applied procedure enabled the preparation of membranes with good compatibility between inorganic and organic components. In terms of the DMFC tests of the composite membranes, working with the cathode feed at 100% r.h., the unmodified sPEEK membrane with SD = 42% proved to have the best performance, although with higher methanol crossover. In contrast, for r.h. of 138%, the best performance was achieved by the sPEEK composite membrane with SD = 68 and 20.0 wt.% of ZrPh and 11.2 wt.% of PBI.

Keywords: Sulfonated poly(ether ether ketone) (sPEEK); Conductivity; Swelling; Pervaporation; Pressure rise method; Direct methanol fuel cell

1. Introduction

The direct (liquid) methanol fuel cell (DMFC) is a promising candidate system for portable electric devices [1–3]. Methanol as an energy carrier has the advantage of having a significant electroactivity and being easily oxidized directly to water and carbon dioxide in catalyst alloys without the need for a reformer. Apart from that, it is easy to handle and transport (liquid at room temperature), can be produced from a variety of sources (natural gas, coal or biogas) and is biodegradable [2].

One of the main obstacles for the development of the DMFC concerns the limitations associated with the usually employed proton exchange membranes [3]. Perfluorinated membranes, such as Nafion® or Flemion®, although very suitable for hydrogen fuel cells, are not appropriate for DMFC applications due to their high methanol and water permeability [4]. Methanol crossover from the anode to the cathode is detrimental for the DMFC performance as it reduces the coulombic efficiency and cell voltage, leading to an efficiency reduction down to 35% [5]. On the other hand, the high water permeability in perfluorinated membranes can cause cathode flooding and, thus, lower cathode performance [6].

In order to improve the performance of the DMFC, it is necessary to develop and test new materials that eliminate or, at least, reduce the reactants loss without decreasing in the same degree the proton conductivity [7]. Non-fluorinated membranes based on the hydrophobic poly(ether ether ketone) (PEEK) have been presented as materials with excellent chemical and mechanical resistance [8–11]. This polymer can be easily made hydrophilic by sulfonation reactions, being the sulfonation degree (SD) controlled by the reaction time and temperature. Recently, Li et al. reported better DMFC performances for the sPEEK membranes (SD = 39 and 47%) compared to Nafion® 115, at 80 °C [12]. In our labs, similar results were obtained for a sPEEK membrane with SD = 42% and thickness ranging from 25 to 55 μm. Non-modified membranes

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resulted to be mechanically instable due to excessive swelling when operated for periods longer than 4 days at medium temperatures (up to 110 °C).

In order to improve the sPEEK membrane properties for DMFC applications at medium temperatures, composite membranes can be prepared by the incorporation of dispersed inorganic proton conductor particles such as α-zirconium phosphate [13–17]. Layered inorganic α-zirconium phosphate is well known for its ion exchange capacity [18,19] and proton conductivity [20–22], depending on its degree of crystallinity, since the protons are mainly transported on the particle surfaces. In order to improve its proton conductivity, the interlayer distance can be increased by the intercalation of alkyldiamines (exfoliation) [23]. These modified zirconium phosphate with increased acidic surface area have been found to have a proton conductivity, at room temperature, that is two or three orders higher than that of the original microcrystal [24]. With this objective in mind and also attempting to improve the compatibility between the sPEEK polymer and the zirconium phosphate particles, the ZrPh dispersion can be treated with *n*-propylamine and further with polybenzimidazole (PBI). Small-angle X-ray scattering (ASAX) and scanning electron microscopy (SEM) results showed that the pretreatment with *n*-propylamine/PBI of the zirconium phosphate dispersion prevents the formation of particles agglomerates and improves the compatibilization between the organic and inorganic phases [25].

The present work focuses on the characterization of composite membranes prepared using sulfonated poly(ether ether ketone) (SD = 42 and 68%) as polymer matrix, which has been modified with different amounts of ZrPh pretreated with *n*-propylamine and PBI. In this study the proton conductivity was evaluated via impedance spectroscopy and DMFC tests were performed at 110 °C and with a cathode inlet feed relative humidity of 100 and 138%.

2. Experimental

2.1. Materials and methods

Sulfonated poly(ether ether ketone) (sPEEK) polymers with sulfonation degrees of 42 and 68% (ion exchange capacity = 1.27 and 1.90 meq/g, respectively) were prepared following the procedure reported in the literature [9–11,26]. Poly(ether ether ketone) was supplied as pellets by Victrex. The sulfonation degree was determined by elemental analysis and by H NMR as described by Nolte et al. [27].

2.2. Preparation of zirconium phosphate

The phosphate dispersion was prepared as described in the US Patent 5,932,361 [28]. Layered α-zirconium phosphate (ZrPh) was synthesised using the method described elsewhere [13], in which $ZrOCl_2$ is used as precursor of ZrO_2. The ZrPh solution (6 wt.% in dimethylformamide, DMF) was treated adding *n*-propylamine solution (1 M in DMF) using the mass relation of 5.7–6.2 g, respectively. After stirring for 3 days the dispersion of treated zirconium phosphate at 60 °C, 6.2 g of polybenzimidazole (PBI) solution (2.5 wt.% in DMF) were added and the dispersion further stirred for 6 days at the same temperature.

2.3. Membrane preparation

The sPEEK polymer was dissolved in dimethylsulfoxide. Then the treated ZrPh dispersion solution was added and the final solution was left to stir for 3 days at 60 °C. After filtration, the solution was cast in a hydrophobised glass plate heated at 70 °C. Next, the membranes were stored in a vacuum oven for 24 h at 90 °C.

2.4. Characterization methods

2.4.1. Proton conductivity

Proton conductivity was determined by impedance spectroscopy with two different cells. With the first cell, the measurements were performed using sulfuric acid (0.33 M) as electrolyte, at 25 °C, and determining the impedance modulus at zero phase shift [16]. The spectrometer used was a HP 4284A, working in the frequency up to 100 Hz. As pretreatment, samples were immersed in water at room temperature during 3 days. One hour before initiating the measurement, the samples were immersed for 1 h in the electrolyte solution.

On the other hand, with the second cell, the measurements were performed using water vapour as described by Alberti et al. [29]. Proton conductivity of the samples without pretreatment was determined at temperatures ranging from 50 to 110 °C and 100% relative humidity. The spectrometer used was a Zahner IM6 electrochemical workstation, working in the frequency range between 10 and 10^6 Hz.

2.4.2. Swelling measurements

Swelling studies were carried out by drying the samples in a vacuum oven at 90 °C for 5 h. After drying, four samples of each membrane were weighed and immersed in deionized water or 20 wt.% aqueous methanol solution and equilibrated for 2 days at each temperature (room temperature, 40, 55 and 70 °C). The weights of the swollen membranes were measured after carefully removing the solution from both surfaces. Membrane swelling (wt.%) was evaluated calculating the ratio between the difference of the wet and dry weight and the dry weight.

2.4.3. Water and methanol pervaporation measurements

The methanol and water permeability coefficients were evaluated by pervaporation measurements as described in [16]. The measurements were performed at 55 °C with a

20 wt.% aqueous methanol solution as feed. Prior to all measurements, samples were immersed in the feed solution for 1 h. The water/methanol selectivity of the composite membranes was obtained dividing the water and methanol permeability coefficients.

2.4.4. Nitrogen/oxygen/carbon dioxide permeability measurements

Nitrogen, oxygen and carbon dioxide permeability coefficients were evaluated at 20 °C using the pressure rise method. The permeation measurements were carried as described by Drioli et al. [30]. Prior to all measurements, membranes were conditioned with the feed stream for 12 h.

2.4.5. Membrane morphology

The membrane morphology was investigated by field emission scanning electron microscopy in a LEO 1550 equipment. Samples were fractured in liquid nitrogen and sputtered with Au/Pd.

2.5. DMFC tests

The membrane electrode assemblies (MEAs) were prepared by hot pressing the membrane samples between two Etek® ELAT electrodes. Supported PtRu (1 mg/cm^2 30 wt.% PtRu(1:1 a/o) on carbon with 0.7 mg/cm^2 Nafion®/PTFE) and Pt (0.4 mg/cm^2 20 wt.% Pt on carbon with 0.7 mg/cm^2 Nafion®/PTFE) were used as anode and cathode electrodes, respectively. The DMFC experimental set-up is described elsewhere [31]. The MEAs (25 cm^2) were fed with an aqueous 1.5 M methanol solution (4 ml/min, 2.5 bar) on the anode side and humidified air (600 sccm/min, 3 bar, 100 and 138% relative humidity) on the cathode side. The MEAs' characterization was performed measuring the DMFC current–voltage polarization curves at 110 °C.

3. Results and discussion

3.1. Proton conductivity

Table 1 shows the effects of the incorporation of zirconium phosphate, pretreated with *n*-propylamine/PBI, in the proton conductivity of the sPEEK polymer at 25 °C in an acid electrolyte (0.33 M H_2SO_4). It can be observed that the proton conductivity of the composite membranes decreases with the amount of inorganic incorporation. The ZrPh treatment with *n*-propylamine was expected to exfoliate the inorganic layers and, consequently, increase the acid surface area and thus the proton conductivity [23]. In a recently published work regarding sPEEK/ZrPh/PBI membranes analysis using SEM and ASAXS techniques [25], it was observed that addition of PBI to a zirconium phosphate dispersion previously treated with *n*-propylamine resulted in ZrPh with some extent of exfoliation. It was also found that the PBI treatment increased the compatibility of the ZrPh particles with the sPEEK polymer and improved the dispersion of the inorganic phase. However, it is believed that with the incorporation of PBI (base) the acid character of the sPEEK/ZrPh/PBI system is lower and, therefore, the proton conductivity may decrease.

Table 1
Proton conductivity of various sPEEK membranes in an acid electrolyte (25 °C in 0.33 M H_2SO_4)

Membrane composition sPEEK/ZrPh/PBI (wt.%)	Thickness (μm)	k_M (mS/cm)
100.0 (SD = 68%)/0/0	75	46.3
84.4 (SD = 68%)/10.0/5.6	73	29.4
68.8 (SD = 68%)/20.0/11.2	84	18.2
100.0 (SD = 42%)/0/0	79	20.2
84.4 (SD = 42%)/10.0/5.6	63	11.5
68.8 (SD = 42%)/20.0/11.2	65	2.8

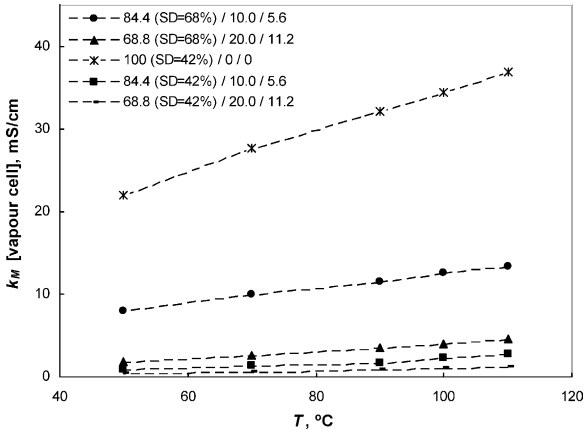

Fig. 1. Proton conductivity of various sPEEK membranes (sPEEK/ZrPh/PBI, wt.%) in the water vapour cell as a function of temperature (at 100% r.h.).

In terms of the membrane conductivity evaluated using the water vapour cell (Fig. 1), a similar trend as for the acid electrolyte cell (Table 1) was observed. The proton conductivity of the pure sPEEK membrane with SD = 68% is not presented because of the high solubility of this polymer and therefore low stability of the unmodified membranes. For the compositions investigated here, the unmodified sPEEK membrane with SD = 42% resulted to be the most conductive membrane. Assuming that conductivity follows the Arrhenius law, it was found that the unmodified membrane presents the lowest proton transport activation energy (Table 2). The introduction of 10 wt.% ZrPh/and 5.6 wt.% PBI caused already a drastic reduction of conductivity.

3.2. Swelling measurements

From Table 3 it can be observed that the membrane swelling in water and methanol aqueous solution (20 wt.%), at room temperature, decreases with the incorporation of pretreated phosphate. However, a slight increase of the

Table 2
Pre-exponential factors, A, and activation energy, E_a, of various sPEEK membranes in the water vapour cell

Membrane composition sPEEK/ZrPh/PBI (wt.%)	A	E_a (kJ/mol)
84.4 (SD = 68%)/10.0/5.6	204.7	11.7
68.8 (SD = 68%)/20.0/11.2	475.1	17.9
100.0 (SD = 42%)/0/0	557.6	11.7
84.4 (SD = 42%)/10.0/5.6	634.3	20.6
68.8 (SD = 42%)/20.0/11.2	152.4	18.5

swelling can be usually noticed when the amount of ZrPh and PBI is increased from 10.0 to 20.0 wt.% and 5.6 to 11.2 wt.%, respectively. From Table 3, it can be also noticed that the swelling in methanol aqueous solution is always higher than in pure water. This fact is even more pronounced for membranes prepared with sPEEK with SD = 42% as polymer matrix.

Fig. 2 shows the swelling of the composite membranes as a function of temperature, when immersed in methanol aqueous solution (20 wt.%). From this plot it can be noticed that swelling increases with temperature for all the studied membranes. The swelling is much higher for unmodified membranes. The unmodified sPEEK membrane with SD = 68% is even soluble at the studied temperatures. For the composite membranes, the highest swelling was observed for the membrane with 10.0 wt.% ZrPh 5.6 wt.% PBI. The results obtained for all composite membranes show improved stability properties in terms of swelling in aqueous methanol solution.

3.3. Permeability towards species present in DMFC (methanol, water and gases)

In terms of membranes permeability towards methanol and water, pervaporation experiments at 55 °C showed that it decreases with the amount of inorganic incorporation for both sulfonation degrees (Table 4). As a matter of fact, the membrane permeability towards water and methanol depends on the solubility and diffusivity of the species in the membrane. There is a good correlation between swelling in methanol aqueous solution (20 wt.%, used as feed in the pervaporation experiments) and the total pervaporation flux, both at 55 °C (Fig. 3). Moreover, it can be also observed that

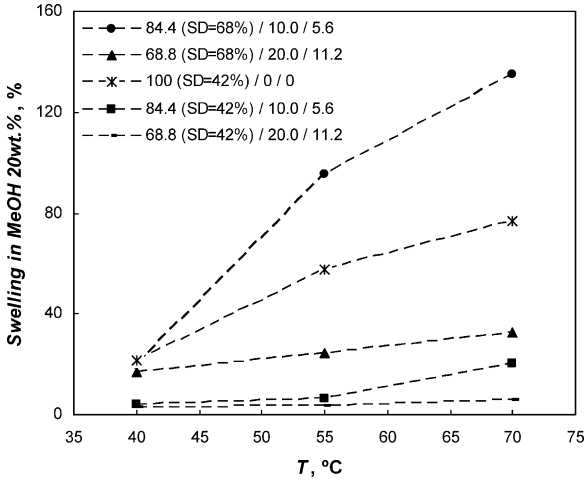

Fig. 2. Swelling in 20 wt.% methanol solution as a function of temperature.

the incorporation of pretreated phosphate leads to an increase of the water/methanol selectivity (Table 4).

On the other hand, gas permeation experiments show that the composite membranes permeability towards nitrogen, oxygen and carbon dioxide decreases with the inorganic phosphate incorporation (Table 5). The values are in all cases low enough to consider the membranes a barrier for the gases. The permeability of CO_2 (and P_{CO_2/N_2}) increased with the sulfonation degree, due to the higher content of acid

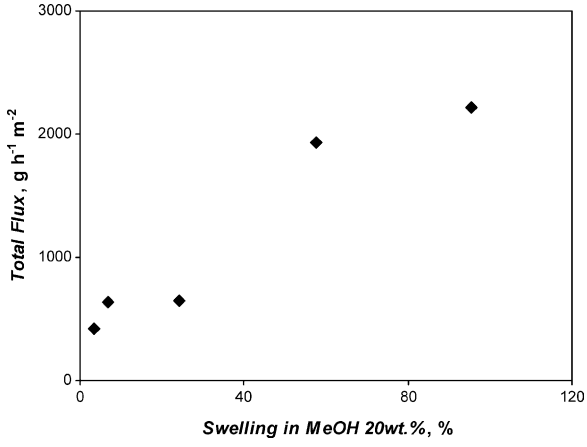

Fig. 3. Total flux from pervaporation measurements at 55 °C as a function of swelling in 20% methanol solution (batch experiments at pervaporation conditions).

Table 3
Swelling of membranes based on sPEEK composites when immersed in water and aqueous methanol (20 wt.%) (batch experiments at room temperature)

Membrane composition sPEEK/ZrPh/PBI (wt.%)	Swelling water (wt.%)	Swelling methanol 20 wt.% solution (wt.%)
100.0 (SD = 68%)/0/0	17.4	–[a]
84.4 (SD = 68%)/10.0/5.6	9.4	11.6
68.8 (SD = 68%)/20.0/11.2	12	13.4
100.0 (SD = 42%)/0/0	10.1	15.0
84.4 (SD = 42%)/10.0/5.6	0.3	4.7
68.8 (SD = 42%)/20.0/11.2	0.6	4.0

[a] Partially soluble.

Table 4
Methanol and water permeability coefficients and water/methanol selectivity of the sPEEK composite membranes (pervaporation experiments at 55 °C with 20 wt.% aqueous methanol solution used as feed, 1 barrer = 10^{-10} cm^3 [STP] cm/(cm^2 s cmHg))

Membrane composition sPEEK/ZrPh/PBI (wt.%)	P_{MeOH} (barrer)	P_{Water} (barrer)	P_{Water}/P_{MeOH}
84.4 (SD = 68%)/10.0/5.6	1.4×10^4	5.2×10^5	37.4
68.8 (SD = 68%)/20.0/11.2	4.7×10^3	2.1×10^5	44.2
100 (SD = 42%)/0/0	2.2×10^4	5.9×10^5	26.6
84.4 (SD = 42%)/10.0/5.6	4.0×10^3	1.3×10^5	32.5
68.8 (SD = 42%)/20.0/11.2	1.5×10^3	9.9×10^4	68.5

Table 5
Nitrogen, oxygen and carbon dioxide permeability coefficients and oxygen/nitrogen and carbon dioxide/nitrogen selectivities of the various sPEEK membranes (pressure rise method at 20 °C with swollen membranes)

Membrane composition sPEEK/ZrPh/PBI (wt.%)	P_{N_2} (barrer)	P_{O_2} (barrer)	P_{CO_2} (barrer)	P_{O_2/N_2}	P_{CO_2/N_2}
100.0 (SD = 68%)/0/0	1.0×10^{-1}	3.5×10^{-1}	7.4	3.5	72.5
84.4 (SD = 68%)/10.0/5.6	4.4×10^{-2}	1.3×10^{-1}	3.2	2.9	75.4
68.8 (SD = 68%)/20.0/11.2	2.7×10^{-2}	6.6×10^{-2}	5.5×10^{-2}	2.5	20.6
100.0 (SD = 42%)/0/0	7.1×10^{-2}	1.4×10^{-1}	2.4	2.0	34.1
84.4 (SD = 42%)/10.0/5.6	3.7×10^{-2}	5.8×10^{-2}	7.9×10^{-1}	1.6	21.3
68.8 (SD = 42%)/20.0/11.2	4.2×10^{-2}	6.2×10^{-2}	6.1×10^{-1}	1.5	14.4

groups. However, the amount of CO_2 crossing the membrane is still very low compared to the methanol transport. It is reasonable to assume that practically all the CO_2 detected in the cathode during DMFC experiments comes from the oxidation of methanol crossing the membrane.

It is well known that the introduction of fillers with low (or none) permeability in a membrane leads to a reduction on the overall membrane permeability when the compatibilization between polymer and filler is good. This reduction is a function of the filler concentration and shape and has been described also previously for gas separation [32]. The interface between filler and polymer matrix is an important factor. In the case of the composite membranes investigated here, PBI strongly interacts with a fraction of the ionic acid groups of the sPEEK polymer and makes the membrane less hydrophilic. Consequently, the barrier properties of the prepared composite membranes increases, which in principle can be assumed as an advantage for DMFC

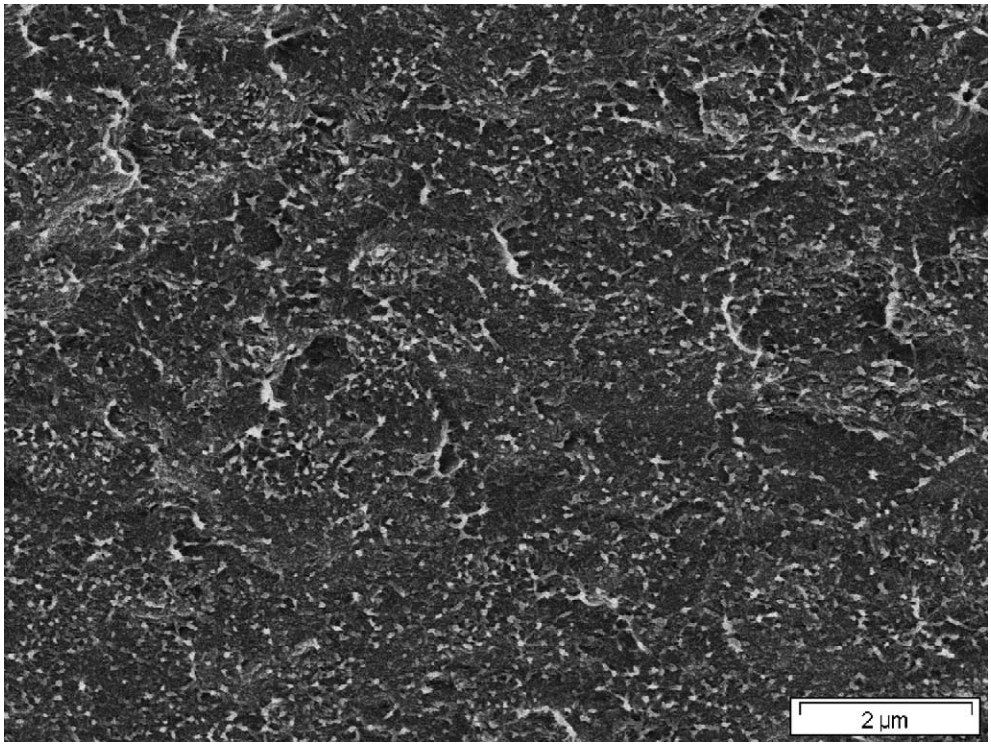

Fig. 4. Scanning electron micrograph of sPEEK (SD = 42%) membrane with 20% ZrPh and 11.2% of PBI.

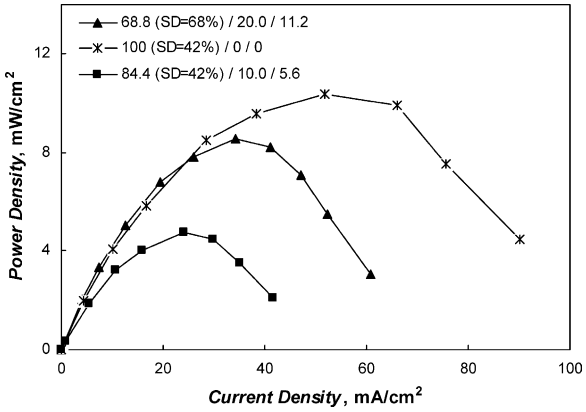

Fig. 5. Power density plots of the DMFC using various sPEEK membranes, at 110 °C and 100% r.h. in the cathode feed.

applications because it reduces the reactants loss and increases the overall fuel cell efficiency.

3.4. Membrane morphology

Fig. 4 shows that the treatment of zirconium phosphate with *n*-propylamine and PBI enabled good compatibility between the inorganic phase and the sPEEK polymer matrix. A reason for this is the basic character of PBI, which enables strong interactions with the acid phosphate particles surface and with the acid sulfonic groups of the sPEEK polymer.

3.5. Polarization curves

The current density/power density plots of MEAs made with the investigated sPEEK composite membranes, at 110 °C and 100% r.h. (cathode feed), are shown in Fig. 5. From these plots it can be observed that the unmodified sPEEK (SD = 42%) membrane presented the maximum power density output. It achieved an output power density value of 10.4 mW/cm^2 for 51.8 mA/cm^2. The unmodified membrane with SD = 68% could not be characterized due to its instability (high swelling or even solubility). However,

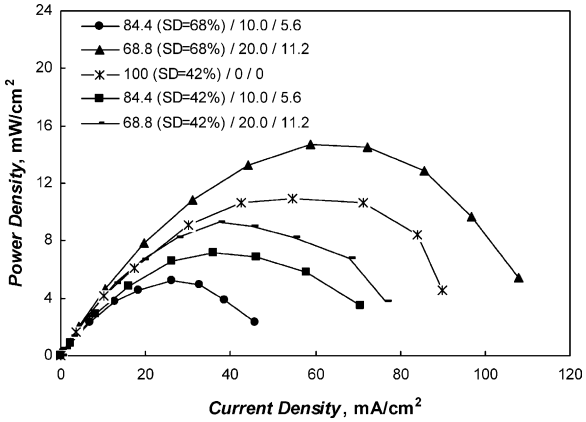

Fig. 6. Power density plots of the DMFC using sPEEK composite membranes, at 110 °C and 138% r.h. in the cathode feed.

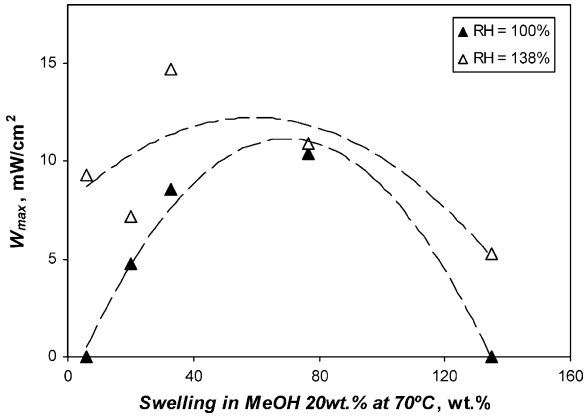

Fig. 7. Maximum power density of the DMFC (110 °C and r.h. of 100 and 138%), as a function of swelling in 20 wt.% methanol solution (lines are guides to the eye), evaluated through batch experiments at 70 °C.

the sPEEK (SD = 68%) membrane with 20.0 wt.% ZrPh and 11.2 wt.% PBI had even higher power density than the membrane with SD = 42% for current densities lower than 25 mA/cm^2. When the relative humidity at the cathode feed was increased to 138% (Fig. 6), it could be observed that the sPEEK (SD = 68%) membrane with 20.0 wt.% ZrPh and 11.2 wt.% PBI had the best performance. This membrane achieved an output power density value of 14.7 mW/cm^2 for 58.8 mA/cm^2. When comparing the plain sPEEK SD = 42% membrane with its composites, for both r.h. values tested, the unmodified membrane had higher power density output. It is worth noting that for the same operation conditions (110 °C and 138% cathode feed r.h.), in terms of amount of CO_2 in the cathode outlet obtained at 35 mV, for the membranes with the best power density output performance (Fig. 6), the membrane with sPEEK (SD = 68%), 20.0 wt.% ZrPh and 11.2 wt.% PBI exhibits a notable value of 0.1 vol.%, in comparison with 1.9 vol.% for the unmodified sPEEK membrane with SD = 42%. However, the filler addition to sPEEK (SD = 42%) besides reducing the crossover had an excessive (negative) effect on the proton conductivity. As a

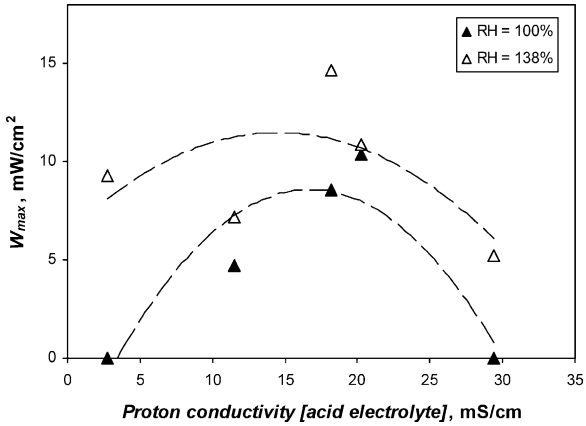

Fig. 8. Maximum power density of the DMFC (110 °C and r.h. of 100 and 138%), as a function of the proton conductivity (lines are guides to the eye), evaluated in acid electrolyte (0.33 M H_2SO_4, impedance spectroscopy at 25 °C).

whole the performance in the DMFC decreased too much after the modification of the low sulfonated membrane.

The maximum output power density is plotted in Fig. 7, for both 100 and 138% r.h., at 110 °C, as a function of the aqueous methanol swelling (evaluated at 70 °C by batch experiments). It can be verified that the plot presents a maximum for both relative humidities. At 100% r.h., both composite membranes with the highest and lowest swelling in methanol present the lowest maximum output power density. This result shows the paramount influence of the membranes swelling in the DMFC performance. Low swelling leads to low proton conductivity (protons transport assisted by sorbed water) and excessive swelling leads to poor DMFC performance (high methanol and water crossover). Moreover, it can be seen that the DMFC performance increases operating at higher cathode feed humidity and, as expected, the performance improvement is higher for the low swelling membranes.

In the particular case of the maximum output power density variation with the proton conductivity evaluated in the acid electrolyte cell, Fig. 8 shows similar results as those obtained for swelling in methanol (Fig. 7). It can be seen that composite membranes with low proton conductivity present low DMFC performance. On the other hand, from Fig. 8 it can be also verified that high proton conductivity does not mean higher DMFC performance, due to the excessive swelling associated to this membranes (higher methanol and water crossover).

4. Conclusions

Composite membranes have been prepared using sPEEK polymer as organic matrix (SD = 42 and 68%) with different contents of zirconium phosphate as inorganic network (10.0 and 20.0 wt.%) pretreated with *n*-propylamine and polybenzimidazole (PBI, 5.6 and 11.2 wt.%).

Impedance measurements showed, for the concentration range investigated, that increasing the ZrPh/PBI content in the sPEEK composite membranes leads to a decrease of the proton conductivity. On the other hand, from impedance characterization it was also observed that the temperature dependence of proton conductivity decreases with the incorporation of inorganic content. In terms of the membranes swelling in water or methanol aqueous solution, batch experiments showed that the inorganic incorporation decreased the swelling of the composite membranes. Moreover, it was observed that the unmodified membrane with SD = 68% was soluble and with SD = 42% had excessive swelling in 20 wt.% aqueous methanol solution, at temperatures higher than 70 °C. This was also the case for composite membranes prepared with sPEEK (SD = 68%) and low inorganic content. All other composite membranes showed improved thermal and chemical stability in the methanol aqueous solution. Pervaporation (H_2O, CH_3OH) and pressure rise (N_2, O_2, CO_2) experiments showed that the incorporation of ZrPh/PBI in the sPEEK polymer organic matrix decreased the DMFC species permeability coefficients. Micrographs obtained by scanning electron microscopy showed a good adhesion between inorganic particles domains and the polymer matrix. Finally, the results obtained from the DMFC tests, at 110 °C, using the prepared composite membranes showed that the best performance was achieved by the unmodified sPEEK membrane (SD = 42%) and sPEEK (SD = 68%) composite membrane containing 20.0 wt.% ZrPh and 11.2 wt.% PBI, for cathode feed relative humidity of 100 and 138%, respectively. For 138% r.h., the DMFC using this composite membrane presented a much lower CO_2 emission (and therefore lower methanol crossover) in the cathode outlet (0.1 vol.%), in comparison with the unmodified sPEEK (SD = 42%) membrane (1.9 vol.%). It is believed that this performance resulted from the best properties of this membrane in terms of swelling in methanol, proton conductivity and water and methanol permeation. Based on the results obtained for the PEM characterization and DMFC tests, among the investigated systems reported here, the incorporation of 20.0 wt.% of ZrPh (pretreated with *n*-propylamine) and 11.2 wt.% of PBI in the sPEEK polymer with SD = 68% was found to be the most favorable for future application in DMFC systems working at temperature up to 110 °C.

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