

# Proton electrolyte membrane properties and direct methanol fuel cell performance

## I. Characterization of hybrid sulfonated poly(ether ether ketone)/zirconium oxide membranes

V.S. Silva<sup>b</sup>, B. Ruffmann<sup>a</sup>, H. Silva<sup>a,b</sup>, Y.A. Gallego<sup>a</sup>, A. Mendes<sup>b,\*</sup>,  
L.M. Madeira<sup>b</sup>, S.P. Nunes<sup>a</sup>

<sup>a</sup> GKSS Research Centre, Max-Planck Str., 21502 Geesthacht, Germany

<sup>b</sup> LEPAE, Chemical Engineering Department, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Received 1 April 2004; received in revised form 15 July 2004; accepted 16 August 2004

Available online 1 October 2004

### Abstract

This paper presents an evaluation of the zirconium oxide effects in sulfonated poly(ether ether ketone) (sPEEK) with sulfonation degree (SD) of 87%. A series of inorganic–organic hybrid membranes were prepared with a systematic variation of the zirconium oxide content via in situ zirconia formation (2.5, 5.0, 7.5, 10, 12.5 wt.%). This procedure enabled the preparation of proton electrolyte membranes (PEM) with a wide range of properties, which can be useful for evaluating the relationship between the PEM properties and the direct methanol fuel cell (DMFC) performance. The investigated properties are the proton conductivity, proton transport resistance, water uptake, water, methanol, oxygen, carbon dioxide and nitrogen permeability coefficients, morphology and elemental analysis. The results obtained show that the inorganic oxide network decreases the proton conductivity and water swelling. It is found that it leads also to a decrease of the water, methanol, carbon dioxide and oxygen permeability coefficients, an increase of the water/methanol selectivity and a decrease of the carbon dioxide/nitrogen and oxygen/nitrogen selectivities. In terms of morphology, it is found that in situ zirconium alkoxide hydrolysis enables the preparation of homogeneous membranes that present a good adhesion between inorganic domains and the polymer matrix.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Sulfonated poly(ether ether ketone) (sPEEK); Zirconium oxide; Sol–gel chemistry; Permeability coefficients; Morphology; Direct methanol fuel cell

### 1. Introduction

In the last decade, the development of the direct methanol fuel cell (DMFC) has gained much interest mainly for portable power applications. It has the advantage of not requiring a fuel processor (more compact and simpler system) and, apart from that, it uses methanol, which has higher energy density compared to hydrogen at high pressures (360 atm) and is easier to handle and transport (liquid

at room temperature) [1]. A DMFC consists in a proton electrolyte membrane (PEM) sandwiched between two porous electrodes containing catalyst. To the fuel cell anode and cathode is fed a solution of methanol (typically 1.5 mol/L) and oxygen (usually as air), respectively.

The PEM plays an important role in the development of the fuel cell technology. In the particular case of the direct methanol fuel cell, it should have a low permeability coefficient for the reactants (mainly methanol), exhibiting high proton conductivity, along with long-term mechanical stability [1]. Species transport through the proton exchange membrane is illustrated in Fig. 1. Although perfluorinated membranes,

\* Corresponding author. Tel.: +351 22 508 1695; fax: +351 22 508 1449.  
E-mail address: [mendes@fe.up.pt](mailto:mendes@fe.up.pt) (A. Mendes).

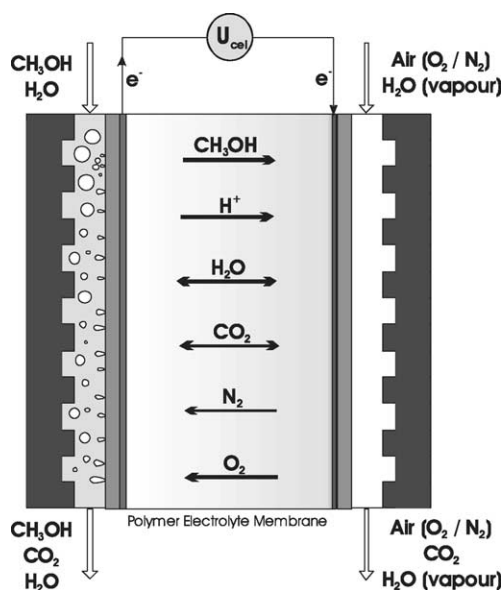


Fig. 1. Sketch of the DMFC illustrating the mass transport of the different species through the proton exchange membrane.

such as Nafion<sup>®</sup> or Flemion<sup>®</sup>, are very suitable for hydrogen fuel cells, they are not suitable for DMFC applications due to their high methanol and water permeability [2]. Methanol crossover from the anode to the cathode reduces the Coulombic efficiency and cell voltage, leading to an overall efficiency reduction [3]. On the other hand, the high water permeability in perfluorinated membranes causes cathode flooding and, thus, lowers the cathode performance [4].

Non-fluorinated membranes based on sulfonated poly(ether ether ketone) (sPEEK) have been presented as promising materials due to their high proton conductivity [5–7]. Furthermore, in order to improve the membrane properties for DMFC applications, the single-phase pure polymer can be modified by the incorporation of a finely dispersed ceramic solid component.

Previous work by our research group focused on the influence of the zirconium oxide incorporation, via hydrolysis, on the proton, water and methanol transport in sulfonated poly(ether ether ketone) with several sulfonation degrees (S.D. = 71 and 87%) [8]. As a result of this study it was observed that the incorporation of increasing amounts of ZrO<sub>2</sub> ranging from 2.5 to 7.5 wt.% in the sPEEK polymer matrix enabled the preparation of membranes with continuously decreasing water swelling, proton conductivity and water and methanol permeation fluxes. No results have been reported regarding DMFC performance using the studied composite membranes with the above-mentioned ZrO<sub>2</sub> content. It was verified that these membranes were not morphologically stable in 20 wt.% aqueous methanol solutions at 60 °C due to excessive swelling (high sulfonation degrees).

The present study aims at expanding the characterization of a series of novel organic–inorganic composite membranes with an extended range of zirconium oxide contents (2.5–12.5 wt.%), from standard characterization methods to

field tests under DMFC conditions. Since the proton conductivity decreases with the amount of ZrO<sub>2</sub>, the sulfonated polymer with the highest sulfonation degree of the previous study (S.D. = 87%) was selected, in order to prepare membranes with enough proton conductivity [8]. Apart from taking advantage of the improved barrier properties of the composite membranes with respect to methanol permeation, the ZrO<sub>2</sub> also increases the membrane morphological stability (lower swelling). Therefore, it enables the use of high sulfonation sPEEK membranes in DMFC applications operating at temperatures up to 90 °C.

## 2. Experimental

### 2.1. Materials and methods

Sulfonated poly(ether ether ketone) (sPEEK) polymers with sulfonation degree of 87% (ion exchange capacity = 2.31 meq/g) were prepared following the procedure reported in the literature [9]. 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. [10].

### 2.2. Membrane preparation

The sPEEK composite membranes were prepared using in situ formation of zirconia with zirconium tetrapropylate as alkoxide and acetyl acetone as chelating agent. First, the sPEEK polymer was dissolved in dimethylsulfoxide (6 wt.% solution) and the incorporation of zirconium oxide was performed as described in detail elsewhere [8]. The water/alkoxide ratio was always maintained higher than 1 to ensure the formation of a finely dispersed inorganic phase in the polymer solution. The mixtures were cast in a hydrophobised glass plate heated to 70 °C for solvent evaporation. Then, the membranes were stored in a vacuum oven for 24 h at 90 °C. The thickness of the prepared membranes with 0.0, 2.5, 5.0, 7.5, 10.0, 12.5 wt.% of zirconium oxide were 188, 175, 133, 146, 128, 106 μm, respectively. Membrane thickness was measured using a Micromaster system by TESA.

### 2.3. Characterization methods

#### 2.3.1. Conductivity

Proton conductivity and proton transport resistance were determined by impedance spectroscopy with two different set-ups, simulating the anode and cathode operation conditions. Both proton conductivity and proton transport resistance values were obtained from the impedance modulus at null phase shift (high frequency side). The proton transport resistance gives the specific resistance of the membrane with respect to proton transport.

The anode environment in the DMFC was simulated experimentally using a liquid acid electrolyte at 25 °C [11]. The electrolyte used was liquid sulfuric acid (0.33 M), ensuring a fully hydrated and protonated state of the measured samples. As pretreatment, samples were immersed in water at room temperature during 3 days to ensure total leaching. One hour before initiating the measurement, the samples were immersed for 1 h in the electrolyte solution. The spectrometer used was a HP 4284A, working in the frequency range between 100 and 10<sup>5</sup> Hz.

On the other hand, the cathode environment in the DMFC was simulated experimentally using water vapour as described by Alberti et al. [12]. Proton conductivity of the samples was determined at temperatures ranging from 50 to 110 °C and 100% relative humidity. The samples were measured without pretreatment. The impedance measurements were carried on stacks containing up to four membranes (similar cumulative thickness, around 430 μm). This procedure was performed because the resistance of a single membrane with low ZrO<sub>2</sub> content (0, 2.5, 5.0 wt.%) is close to the short-circuited cell's resistance. Obviously, the measured conductivity for the all stack is affected by the contact resistance between the membranes. The evaluation of the material resistance was performed subtracting such effect, as described by Alberti et al. [12]. The stacks were pressed between two Etek<sup>®</sup> electrodes to decrease the mass and charge transfer resistance between the membrane and the cell electrodes. The spectrometer used was a Zahner IM6 electrochemical workstation, working in the frequency range between 10 and 10<sup>6</sup> Hz.

### 2.3.2. Water swelling

Water swelling studies were performed in batch experiments at room temperature as described elsewhere [8]. Relative water uptake (%) was evaluated calculating the ratio between the difference of the wet and dry weight and the dry weight of the membranes.

### 2.3.3. Water and methanol pervaporation measurements

Water and methanol permeability coefficients were evaluated from pervaporation measurements at 55 °C with a 20 wt.% methanol solution. The pervaporation set-up is described elsewhere [13]. The evaluation of the permeability coefficients was performed using the method described in detail elsewhere [2]. The water/methanol selectivity of the composite membranes was obtained as the ratio between water and methanol permeability coefficients. Prior to all measurements, samples were immersed in deionized water at room temperature for 3 days.

### 2.3.4. Nitrogen/oxygen/carbon dioxide permeability coefficients 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. [14]. The feed gas was previously humidified

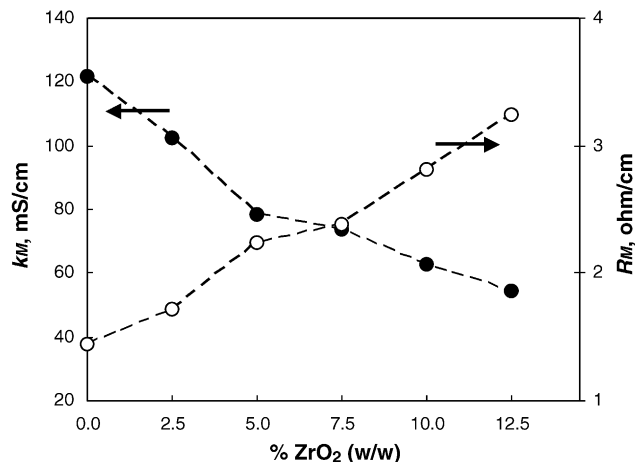


Fig. 2. Proton conductivity and impedance resistance of the sPEEK composite membranes in an acid electrolyte as a function of the ZrO<sub>2</sub> content (25 °C in 0.33 M H<sub>2</sub>SO<sub>4</sub>).

and fed to a Millipore cell with a 47 mm membrane diameter. The pressure in the permeate vessel was measured using a 100 mbar pressure sensor. Experiments were stopped when the permeate pressure was 25 mbar (for fast permeation species) or after 15 h (for slow permeation species). Prior to all measurements, membranes were conditioned with the feed stream for 12 h. This procedure ensured that membranes were in the swollen stationary state.

### 2.3.5. Membrane morphology

The membrane morphology was investigated by field emission scanning electron microscopy in a LEO equipment, using both secondary and backscattered electron detectors. Samples were fractured in liquid nitrogen and sputtered with carbon in a penning sputtering equipment.

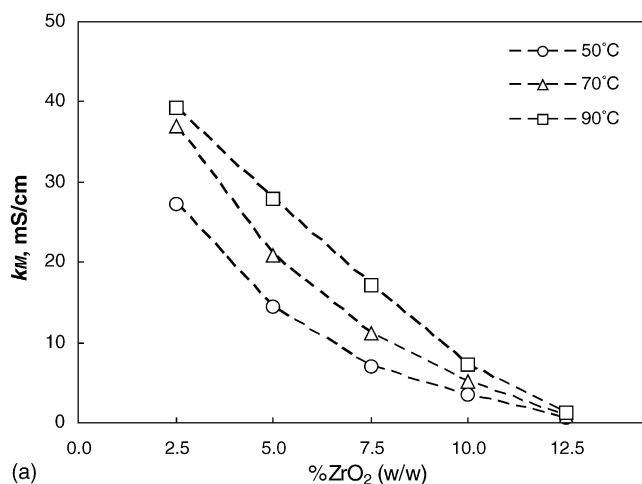
### 2.3.6. Membrane elemental analysis

The membrane elemental analysis was investigated by X-ray microfluorescence (XRMF) in an EDAX spectrometer. The samples were fractured in liquid nitrogen and sputtered with palladium in a penning sputtering equipment.

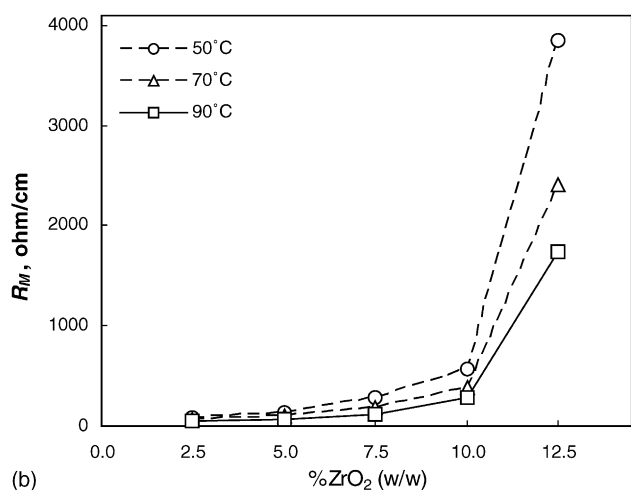
## 3. Results and discussion

### 3.1. Proton conductivity

Fig. 2 shows the effects of the zirconium oxide incorporation in the sPEEK polymer on the proton conductivity and proton transport resistance measured at 25 °C in an acid electrolyte (set-up 1, 0.33 M H<sub>2</sub>SO<sub>4</sub>). The proton conductivity of the composite membranes decreases continuously with the inorganic content. The opposite behavior can be observed for the membrane resistance. In terms of the membrane conductivity evaluated in the water vapour cell (set-up 2, Fig. 3a), it can be seen that the proton conductivity also decreases with the amount of zirconium oxide. Furthermore, as observed for



(a)



(b)

Fig. 3. Proton conductivity (a) and impedance resistance (b) of the sPEEK composite membranes in water vapor as a function of the ZrO<sub>2</sub> content (100% r.h.).

the acid electrolyte cell, it can be seen that the proton transport resistance increases with the amount of inorganic filler (Fig. 3b). It is worth noting that for the membrane with the highest content of inorganic incorporation (12.5 wt.% ZrO<sub>2</sub>), the resistance becomes very high. As expected, proton conductivity increases with temperature while resistance shows the opposite trend.

These results can be attributed to the possible chemical influence of the polymer functional groups nature in the inorganic oxide phase growth. As stated by Mauritz [15], it can be assumed that the hydrolysis reaction is catalyzed via pendant  $-\text{SO}_3^- \text{H}^+$  groups and, therefore, due to energetic preferences, the hydrolyzed alkoxides would preferentially migrate to the preformed membrane polar clusters. Consequently, the amount of sorbed electrolyte will be smaller (water vapour or aqueous sulfuric acid), decreasing the proton conductivity assisted by water [16]. However, the decrease of the proton conductivity is believed to derive mainly from the increased barrier properties of the membranes due to the incorporation of inorganic fillers [17].

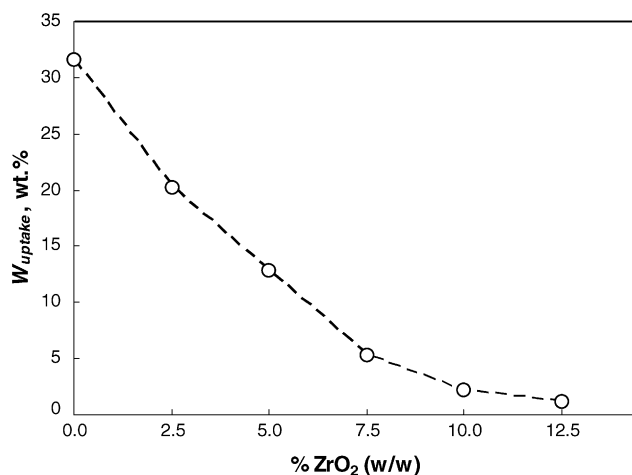


Fig. 4. Water uptake of sPEEK composite membranes as a function of the ZrO<sub>2</sub> content (room temperature).

### 3.2. Water uptake

From Fig. 4 it can be observed that, for the studied membranes, water uptake decreases to very low levels with the zirconium oxide incorporation. The observed variation is more pronounced for the lower ZrO<sub>2</sub> contents. Comparing the water uptake results (Fig. 4) and the corresponding proton conductivity (Figs. 2 and 3), it can be observed that higher water uptake leads to higher proton conductivity, showing the importance of sorbed water in the proton conductivity of sulfonated membranes, in agreement with previous studies [16]. However, it seems that for the acid electrolyte cell, a reduced water uptake does not mean reduced conductivity as it occurs for the water vapour cell. This fact shows that low sulfuric acid uptake leads to enough proton conductivity for the proton electrolyte membrane. In contrast, due to the absence of protons in the water vapour cell, the conductivity decreases to very low values due to the low sorbed water in the polymer polar channels.

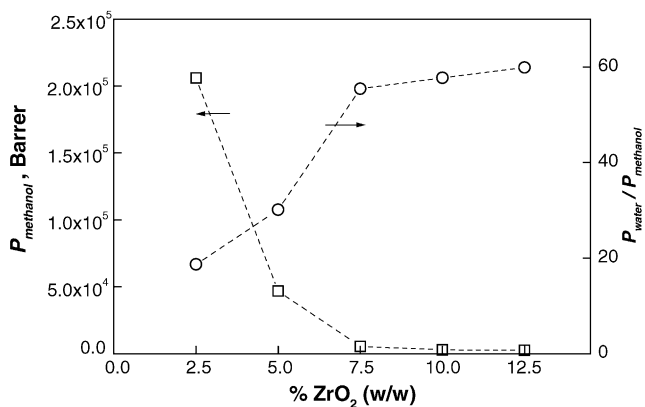


Fig. 5. Methanol permeability coefficients and water/methanol selectivity of the sPEEK composite membranes as a function of the ZrO<sub>2</sub> content (pervaporation experiments at 55 °C, 1 Barrer = 10<sup>-10</sup> cm<sup>3</sup> [STP] cm/(cm<sup>2</sup> s cmHg)).

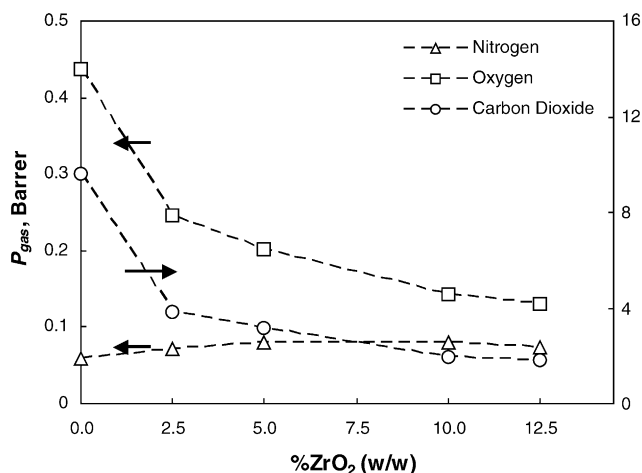


Fig. 6. Nitrogen, oxygen and carbon dioxide permeability coefficients of sPEEK composite membranes as a function of the ZrO<sub>2</sub> content (pressure rise experiments at 20 °C).

### 3.3. Permeabilities towards species present in DMFC

Pervaporation experiments at 55 °C showed that the membranes permeability towards methanol decreases with the amount of zirconium oxide (Fig. 5). As observed previously for the water uptake and proton conductivity (vapour cell) properties, at lower ZrO<sub>2</sub> contents the effects in the permeability coefficients of water and methanol are much more pronounced. Moreover, from Fig. 5, it can be observed that the zirconium oxide content leads to an increase in the water/methanol selectivity.

The membrane permeability towards nitrogen, oxygen and carbon dioxide as a function of the zirconium oxide content is given in Fig. 6. It can be observed that the oxygen and carbon dioxide permeability coefficients decrease with the amount

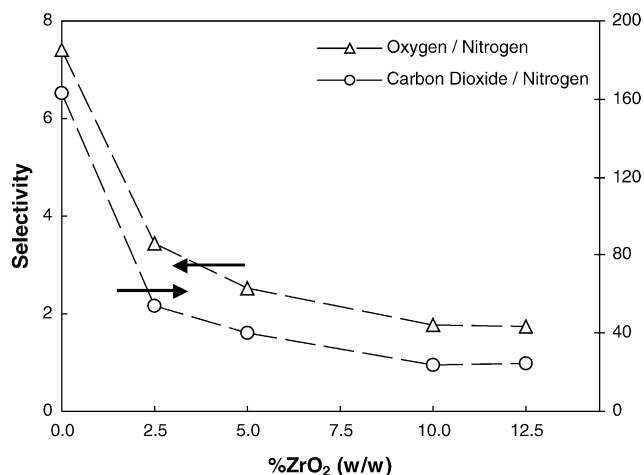


Fig. 7. Oxygen/nitrogen and carbon dioxide/nitrogen selectivities of the sPEEK composite membranes as a function of the ZrO<sub>2</sub> content (pressure rise experiments at 20 °C).

of ZrO<sub>2</sub>. In contrast, the inorganic modification resulted to have no noticeable effect on the nitrogen permeability coefficient. It seems that the less hydrophilic behavior of the higher ZrO<sub>2</sub> content composite membranes results in lower permeability towards oxygen and carbon dioxide. It can be also noticed that the carbon dioxide permeability coefficient in the sPEEK composite membranes is much higher than that of oxygen or nitrogen. This fact can be explained by the higher 'interactive' behavior of CO<sub>2</sub> with the polymer's polar groups and sorbed water. Fig. 7 shows that the oxygen/nitrogen and carbon dioxide/nitrogen selectivities decrease with the ZrO<sub>2</sub> content. These results are in agreement with previous data for DMFC species mass transfer in sPEEK polymer with several sulfonation degrees [14]. In that study, lower sPEEK sulfonation degrees resulted in lower hydrophilicity, lower wa-

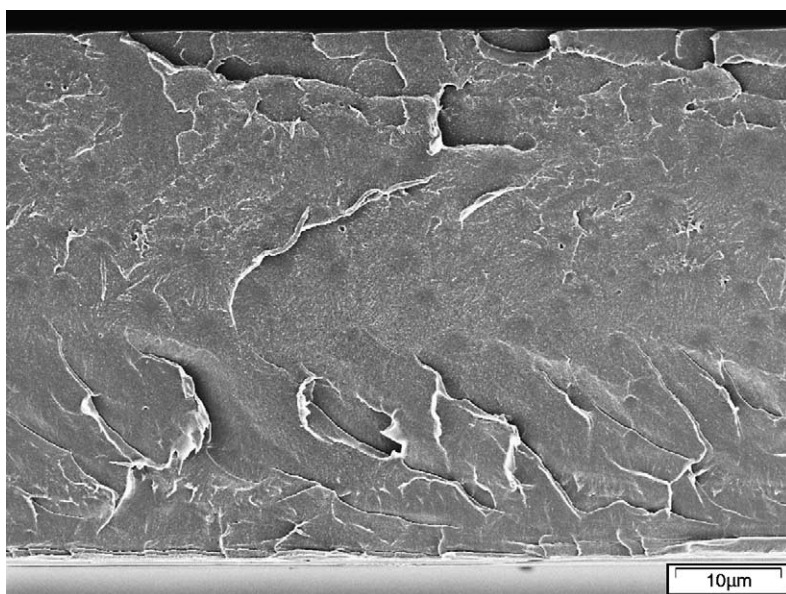


Fig. 8. Scanning electron micrograph of sPEEK composite membranes with 2.5 wt.% of ZrO<sub>2</sub>.

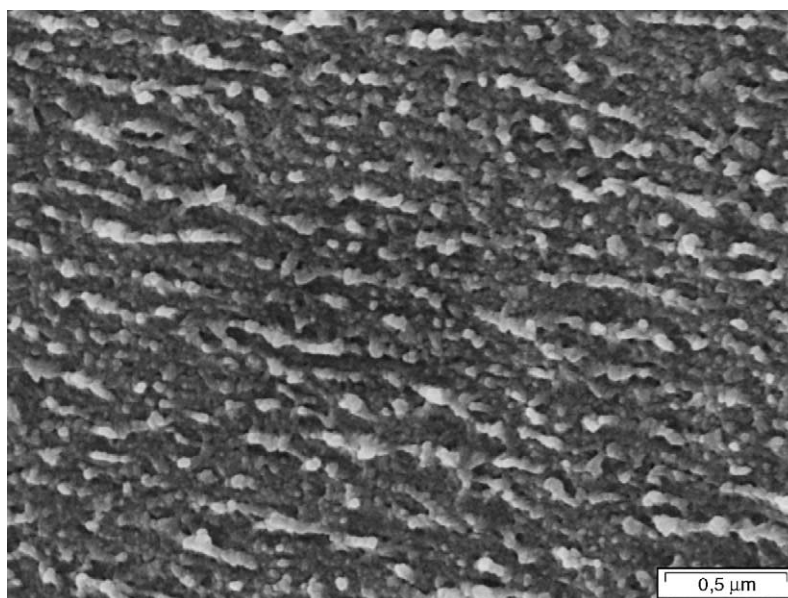


Fig. 9. Scanning electron micrograph showing the  $\text{ZrO}_2$  particles finely dispersed in the sPEEK composite membrane with 5 wt.% of  $\text{ZrO}_2$ .

ter uptake and, finally, lower permeability towards  $\text{CO}_2$  and  $\text{O}_2$ . Therefore, the decreasing sorbed water by the polymer (Fig. 4) seems to decrease the oxygen/nitrogen and carbon dioxide/nitrogen selectivity. Additionally, it can be observed that the carbon dioxide/nitrogen selectivity is much higher compared with that corresponding to oxygen/nitrogen.

The reduced permeability towards DMFC species of the  $\text{ZrO}_2$  modified composite membranes is believed to derive from the weaker hydrophilicity of the polymer, higher concentration of rigid backscattering sites and increased tortuous pathways that molecules encounter during permeation due to the presence of inorganic particles [17]. Consequently, the barrier properties of the membranes increases with the  $\text{ZrO}_2$  content, which can be assumed as an advantage for DMFC applications because it reduces the reactants loss and increases the overall fuel cell efficiency. Nevertheless, the verified proton conductivity decrease with the incorporation of  $\text{ZrO}_2$  should be also taken in account. Finally, according to the results presented for proton conductivity, water uptake and liquid and gas permeability coefficients, it seems that these properties depend on the same transport phenomena.

#### 3.4. Microscopy and elemental analysis

Fig. 8 shows that the prepared membranes can be considered as homogeneous and dense (composite membrane with 2.5 wt.%  $\text{ZrO}_2$ ). Higher magnification electron micrograph shows a good adhesion between inorganic domains and the polymer matrix (Fig. 9). It can be observed that no cavities are present and that the  $\text{ZrO}_2$  particles have dimensions smaller than  $\sim 100$  nm.

Elemental analysis was performed by EDAX, in order to evaluate the effective incorporation of zirconium oxide on the composite membranes after the preparation procedure (mix-

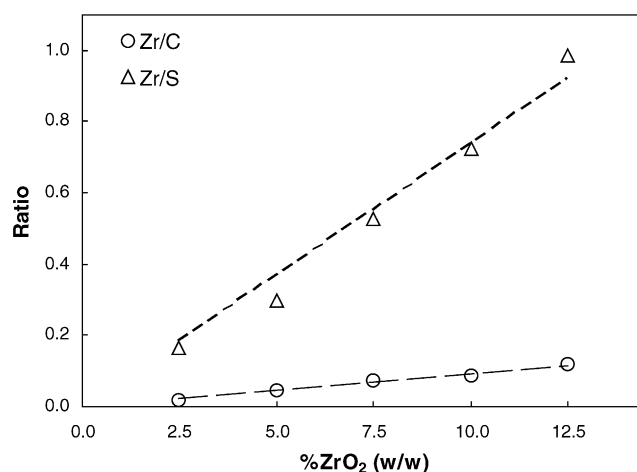


Fig. 10. Ratio between zirconium and carbon or sulfur contents of the sPEEK composite membranes as a function of the  $\text{ZrO}_2$  content (elemental analysis by EDAX X-ray microfluorescence).

ing, filtration and casting). The analysis of the elemental content ratios between zirconium and carbon or sulfur (Fig. 10) shows that both ratios increase linearly with the increased zirconium oxide content in the membrane.

#### 4. Conclusions

Composite membranes have been prepared using sPEEK polymer as organic matrix (S.D. = 87%) with different contents of zirconium oxide in the inorganic network (2.5, 5.0, 7.5, 10, 12.5 wt.%). Proton conductivity, water uptake, permeability towards species present in DMFC operation ( $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$ ), morphology and elemental analysis of each membrane were obtained by standard characterization methods.

The results showed that increasing the zirconium oxide content in the sPEEK composite membranes leads to a decrease of the reactants permeability coefficients (except for nitrogen) and an increase of the water/methanol selectivity. The reason for these results is related with the increasing amount of inorganic filler in the membranes, which increases the membranes barrier properties in terms of mass transport. These features are advantages for the direct methanol fuel cell performance because they prevent reactants loss and increase the PEM long-term stability. However, results showed that the zirconium oxide modification has the detrimental effect of decreasing the proton conductivity. The micrographs obtained by scanning electron microscopy showed a good adhesion between inorganic particles domains and the polymer matrix (no cavities) and that the particles have dimensions smaller than  $\sim 100$  nm. On the other hand, elemental analysis performed by EDAX showed that elemental content ratios between zirconium and carbon or sulfur increase in agreement with the increased zirconium oxide amount in the membrane. These results ensured that even after the complex preparation procedure (among others, filtration and solvent evaporation), the zirconium oxide content varied according to what was planned.

Furthermore, the different contents of zirconium oxide in the sPEEK polymer organic matrix enabled the preparation of composite membranes with a wide range of properties concerning proton conductivity, water uptake and methanol and water permeation. Therefore, these membranes can be used in the future to make a critical evaluation of the relationship between the proton electrolyte membrane properties and the DMFC performance. This will be discussed in part II of this paper.

### Acknowledgements

Financial support by the HGF-Vernetzungsfonds is gratefully acknowledged. The authors wish to thank M. Schossig-Tiedemann and M. Adherhold for making the microscope analysis and Dr. S. Vetter for sulfonating the poly(ether ether ketone) polymer. The work of Vasco Silva and Hugo Silva was supported by FCT (grants SFRH/BD/6818/2001 and SFRH/3029/2000, respectively). Vasco Silva would like also to acknowledge both FCT and GKSS for the grant assigned for his stay at GKSS Forschungszentrum GmbH. The present work was in part supported by FCT/FEDER projects POCTI/EQU/38075/2001 and POCTI/EQU/45225/2002.

### References

- [1] L. Jörissen, V. Gogel, J. Kerres, J. Garche, New membranes for direct methanol fuel cells, *J. Power Sources* 105 (2002) 267.
- [2] C. Manea, M. Mulder, Characterization of polymer blends of polyethersulfone/sulfonated polysulfone and polyethersulfone/sulfonated polyetheretherketone for direct methanol fuel cell applications, *J. Membr. Sci.* 206 (2002) 443.
- [3] F.R. Kalhammer, P.R. Prokopius, V.P. Voecks, Status and prospects of fuel cells as automobile engines, State of California Air Resources Board, California, 1998.
- [4] J. Cruickshank, K. Scott, The degree and effect of methanol crossover in the direct methanol fuel cell, *J. Power Sources* 70 (1998) 40.
- [5] S.M.J. Zaidi, S.D. Mikailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, Proton conducting composite membranes for polyether ether ketone and heteropolyacids for fuel cell applications, *J. Membr. Sci.* 173 (2000) 17.
- [6] S.D. Mikhailenko, S.M.J. Zaidi, S. Kaliaguine, Sulfonated polyether ether ketone composite polymer electrolyte membranes, *Catal. Today* 67 (2001) 225.
- [7] T. Kobayashi, M. Rikukawa, K. Sanui, N. Ogata, Proton-conducting polymers derived from poly(ether-etherketone) and poly(4-phenoxybenzoyl-1,4-phenylene), *Solid State Ionics* 106 (1998) 219.
- [8] V. Silva, B. Ruffmann, H. Silva, A. Mendes, M. Madeira, S. Nunes, Zirconium oxide modified sulfonated poly(ether ether ketone) membranes for direct methanol fuel cell applications, *Mater. Sci. Forum* 455–456 (2004) 587.
- [9] M.C. Wijers, Supported liquid membranes for removal of heavy metals, Dissertation, University of Twente, The Netherlands, 1996.
- [10] R. Nolte, K. Ledjeff, M. Bauer, R. Mulhaupt, Partially sulfonated poly(arylene ether sulfone) – a versatile proton conducting membrane material for modern energy conversion technologies, *J. Membr. Sci.* 83 (1993) 211.
- [11] B. Ruffmann, H. Silva, B. Schulte, S. Nunes, Organic/inorganic composite membranes for application in DMFC, *Solid State Ionics* 162/163 (2003) 269.
- [12] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, Polymeric proton conducting membranes for medium temperature fuel cells (110–160 °C), *J. Membr. Sci.* 185 (2001) 73.
- [13] S.P. Nunes, B. Ruffmann, E. Rikowsky, S. Vetter, K. Richau, Inorganic modification of proton conductive polymer membranes for direct methanol fuel cells, *J. Membr. Sci.* 203 (2002) 215.
- [14] E. Drioli, A. Regina, M. Casciola, A. Olivetti, F. Tratta, T. Massari, Sulfonated PEEK-WC membranes for possible fuel cell applications, *J. Membr. Sci.* 228 (2004) 139.
- [15] K.A. Mauritz, Organic-inorganic hybrid materials: perfluorinated ionomers as sol-gel polymerization templates for inorganic alkoxides, *Mater. Sci. Eng. C* 6 (1998) 121.
- [16] K.A. Kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, *J. Membr. Sci.* 185 (2001) 3.
- [17] B. Kumar, J.P. Fellner, Polymer-ceramic composite protonic conductors, *J. Power Sources* 123 (2003) 132.