Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Pre-treatment Effect on the Sulfonated Poly(ether ether ketone) Membrane Transport Properties and Direct Methanol Fuel Cell Performance

V. S. Silva[a]; V. B. Silva[a]; A. Mendes[a]; L. M. Madeira[a]; H. Silva[ab]; J. Michaelmann[b]; B. Ruffmann[b]; S. P. Nunes[b]
[a] LEPAE, Faculty of Engineering, Chemical Engineering Department, University of Porto, Porto, Portugal [b] GKSS Research Centre, Geesthacht, Germany

To cite this Article Silva, V. S. , Silva, V. B. , Mendes, A. , Madeira, L. M. , Silva, H. , Michaelmann, J. , Ruffmann, B. and Nunes, S. P.(2007) 'Pre-treatment Effect on the Sulfonated Poly(ether ether ketone) Membrane Transport Properties and Direct Methanol Fuel Cell Performance', Separation Science and Technology, 42: 13, 2909 — 2925

To link to this Article: DOI: 10.1080/01496390701558342

URL: http://dx.doi.org/10.1080/01496390701558342

Separation Science and Technology, 42: 2909–2925, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701558342

Pre-treatment Effect on the Sulfonated Poly(ether ether ketone) Membrane Transport Properties and Direct Methanol Fuel Cell Performance

V. S. Silva, V. B. Silva, A. Mendes, and L. M. Madeira
LEPAE, Faculty of Engineering, Chemical Engineering Department,
University of Porto, Porto, Portugal

H. Silva
LEPAE, Faculty of Engineering, Chemical Engineering Department,
University of Porto, Porto, Portugal and GKSS Research Centre,
Geesthacht, Germany

J. Michaelmann, B. Ruffmann, and S. P. Nunes
GKSS Research Centre, Geesthacht, Germany

Abstract: In this paper a critical study is presented on how the direct methanol fuel cell (DMFC) membrane properties are affected by a pre-treatment. Membranes based on sulfonated poly(ether ether ketone) (sPEEK) with sulfonation degree (SD) of 42% were used, plain and modified inorganically with 1 wt.% of zirconium oxide. Nafion® 1135 was used as reference. The results obtained show that the sPEEK polymer (SD = 42%) enables the preparation of proton exchange membranes with improved properties compared to Nafion® and to the ZrO_2-modified sPEEK membrane, mainly due to its improved relation between proton conductivity and methanol permeation. After the pre-treatment, the plain sPEEK membrane had a performance 6.4 times higher in terms of maximum power output when used in the DMFC.

Keywords: Sulfonated poly(ether ether ketone) (sPEEK), nafion, conductivity, pervaporation, permeability coefficients and direct methanol fuel cell

Received 9 November 2006, Accepted 18 May 2007

Address correspondence to A. Mendes, LEPAE, Faculty of Engineering, Chemical Engineering Department, University of Porto, 4200-465 Porto, Portugal. Tel.: + 351 22 508 1695; Fax: +351 22 508 1449; E-mail: mendes@fe.up.pt

INTRODUCTION

Liquid feed direct methanol fuel cells (DMFCs) operating at low temperatures and employing solid protonic electrolytes are promising candidates for portable power applications (1). Actually, DMFCs do not require fuel processing, allowing simple and compact designs (Fig. 1). Apart from that, the use of methanol as fuel for portable applications has several advantages in comparison with hydrogen. But in order to be competitive within the portable power applications market, the DMFC must be economical and capable of delivering high power densities (2). However, the use of the well-known perfluorinated membranes as polymer electrolyte significantly increases the cost of the entire system (3, 4). Besides the cost disadvantage, the use of Nafion®-like polymer electrolyte leads to a significant decrease in the fuel cell Faraday efficiency due to methanol crossover from the anode to the cathode. Consequently, methanol competes with oxygen for the cathode Pt sites (reducing the effective catalyst area), generating a mixed potential that reduces the cell voltage (5, 6). Nevertheless, these problems can be mitigated by developing new polymers, or modifying existing ones, in order to achieve high ionic conductivity, low permeability towards DMFC reactants, long-term stability under operating conditions and, not less important, low cost. Nowadays, non-perfluorinated polymers meet some of these criteria, and are therefore investigated by different groups (7–12). These polymers can be modified or directly applied to the DMFC, either using organic or inorganic additives, so that the properties of the final proton exchange membranes can be improved (9, 10, 13–15).

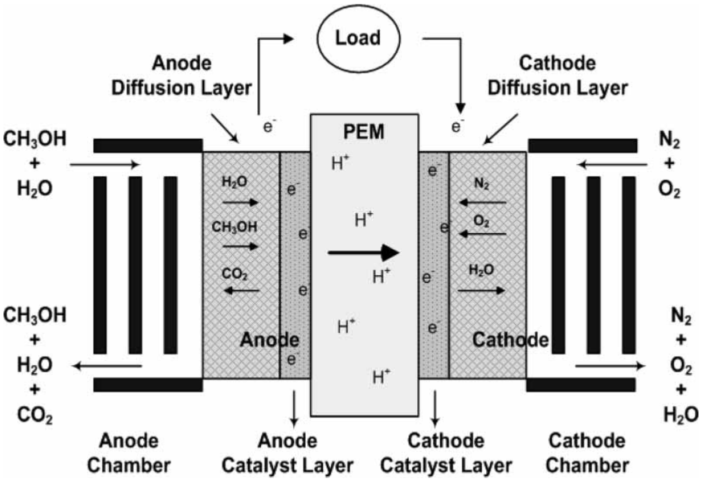

Figure 1. Sketch of a DMFC illustrating the species transport.

Non-fluorinated membranes based on sulfonated poly (ether ether ketone) (sPEEK) have been presented as promising materials due to their high proton conductivity (8, 9, 13, 16) and easy sulfonation of the PEEK polymer. In order to further 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 groups focused on the influence of the zirconium oxide incorporation, via hydrolysis, on the proton, water, and methanol transport in sPEEK with several sulfonation degrees (13, 16).

On the other hand, when a membrane-electrode assembly (MEA) is put to work for the first time in a DMFC shows a significantly lower performance than after some activation procedures (17, 18). The pre-treatment of the membrane aims to reduce these activation procedures and to attain the highest performance. Moreover, when a DMFC is started after being stopped for some time its performance might be lower than before. This phenomenon is mostly related to the membrane water content decrease (dehydration) and is typical in polymer electrolyte membrane. Procedures to bring the membrane to its highest performance are also known as activation procedures.

Therefore, it is important to develop a more efficient methodology of membrane pre-treatment in order to achieve the highest DMFC performance as fast as possible. Several papers discuss different strategies for pre-treating the MEA. Some concentrate their attention mainly on the electrodes, while others focus also on the membrane. For instance, it is reported that the pre-treatment of electrodes and catalyst-coated membranes with acetic acid leads to an increased catalytic activity compared to the untreated counterparts (19). This activation is related to the electrode's ability to retain water within the catalyst layer. The improvement of the PEMFC performance was also tried via nitric acid treatment of the MEA (20). Nitric acid seems to be able to increase the wettability and proton conductivity on the surface of carbon particles, allowing enhanced performance of the MEA (20). On the other hand, Kho et al. (17) found that the DMFC performance was significantly influenced by the exposure of the membrane-electrode assembly either to water or to a methanol solution prior to use. The improvement in the performance was intimately related to the achievement of higher levels of hydration, both in the membrane and the electrodes. Another activation process suggests exposing the MEA to high temperatures and pressuring it (21). It seems that this procedure is able to reduce the ionic resistance, which includes both membrane resistance and catalyst layer resistance. It is proposed that the catalyst active area is increased by opening many "dead" regions. These dead regions are catalyst sites which were hindered, not allowing the contact with the reactants before the activation protocol. Nafion regions near the catalyst sites, which are not well hydrated, can also be seen as dead spots. The effect is claimed to be long-lasting.

The membrane immersion on water at high temperatures or boiling water is a typical procedure for pre-treating the membranes. In particular, it allows to increase the ionic conductivity (σ) of sulfonated PEEK membranes at low temperatures ($<100^\circ$C) and to decrease the temperature-dependence of σ, this behavior being intimately related with the degree of hydration (22). However, as far as we know, there is not any systematic and detailed published study that evaluates the pre-treatment effect on the fluorinated/non-fluorinated membrane properties. So, the present study aims to characterize sPEEK membranes, plain and loaded with ZrO_2, and to perform a critical study regarding the pre-treatment effects on the properties of the membranes and on the DMFC performance. Nafion® 1135 was used as reference material.

EXPERIMENTAL

Materials and Methods

Poly(ether ether ketone) (sPEEK) was supplied as pellets by Victrex and sulfonated in our laboratories as described in the literature (23). After preparation, the polymer was washed in a 20 wt.% aqueous methanol solution for two weeks in order to dissolve the sPEEK chains with higher sulfonation degrees. We believe that this procedure ensures improved morphological stability of the polymer during DMFC application. The final sulfonation degree obtained was 42% (ion exchange capacity, IEC, of 1.27 meq/g), which was determined by elemental analysis and by H-NMR. Zirconium tetrapropylate (70 wt.% solution in iso-propanol) and acetyl acetone (ACAC) were purchased from Gelest. Commercially available Nafion® 1135 was purchased from Aldrich.

Membrane Preparation

Sulfonated poly(ether ether ketone) polymer was dissolved in dimethylsulfoxide (5%, w/w) and left to stir for one day. The membrane with 1 wt.% of zirconium oxide was prepared by in situ sol-gel chemistry as described by Silva et al. (16), growing a finely dispersed inorganic phase in the polymer solution. Zirconium tetrapropylate, $Zr(OPr)_4$, was used as a precursor of the inorganic zirconium oxide modification (16) and acetyl acetone was used as chelating agent to avoid the precipitation of the inorganic compound. The final pure sPEEK and composite sPEEK/zirconium oxide solutions were cast in a hydrophobized glass plate heated to 70°C. After casting, the membranes were stored in a vacuum oven for 24 hours at 90°C.

Membrane Pre-treatment

As pre-treatment, membranes samples were immersed in boiling water for 1 hour, one day before the characterization. Membrane thickness was measured using a micrometer (Digital Micromaster, Brown & Shap) before and after the pre-treatment.

Characterization Methods

Proton Conductivity

Conductivity experiments were carried out at 25°C in a polycarbonate cell described elsewhere (24), using ac impedance spectroscopy and an acid electrolyte (0.33M sulphuric acid). Basically, a membrane sample with ca. 5.68 cm^2 was placed in the above-mentioned aqueous electrolyte solution between two platinum electrodes, which have a diameter of 2.8 cm and a distance between them of about 2 mm. The polycarbonate cell consists of two different compartments, each one with a terminal to connect the probes for electrochemical characterization. One hour before the measurement the samples were immersed in the electrolyte solution. The spectrometer used was a HP 4284A working in the frequency range between 100 and 10^5 Hz.

Swelling Measurements

Swelling studies were carried out by drying the samples in a vacuum oven at 90°C for 5 hours. After drying, four samples of each membrane were weighted and immersed in deionized water, 1.5 or 6.0 M aqueous methanol solution and equilibrated for 2 days at different temperatures (40, 55, and 70°C). This ensures that the equilibrium was attained. 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.

Permeability Measurements

The methanol permeability coefficients were evaluated from pervaporation measurements (24). Briefly, the set-up considers a permeation cell where the permeate side is under vacuum (<1 mbar) and the retentate side contacts the feed aqueous solution. During the experimentation, the permeate is collected in a U-shaped tube immersed in liquid nitrogen. On the other hand, the retentate stream is recycled to the feed tank which should be large enough to prevent concentration variations due to the selective permeation. The experiments were run for approximately 2–3 h, ensuring that the permeate volume collected represents the steady state conditions, at 40, 55, and 70°C with the same membrane sample and with a 6.0M aqueous methanol solution. Prior to all measurements, samples were immersed in the feed solution for 1 hour. The water/methanol selectivity of the composite membranes was obtained dividing the water and methanol permeability coefficients.

DMFC Tests

The membrane electrode assemblies (MEAs) were prepared by hot pressing the membrane samples between two Etek® ELAT electrodes at 85°C and 74 bar for 2 minutes. PtRu (0.5 mg/cm^2 of 20 wt.% PtRu (1:1) catalyst supported on carbon with 0.7 mg/cm^2 Nafion®/PTFE) and Pt (0.5 mg/cm^2 of 30 wt.% Pt catalyst on carbon with 0.7 mg/cm^2 Nafion®/PTFE) were used as anode and cathode electrodes, respectively. Low loads of noble metals were employed in the electrodes in order to allow a more effective evaluation of the membranes concerning the methanol crossover. The DMFC experimental set-up consists basically on two feed supplying systems, a controlling system and the fuel cell, which is placed inside an oven for temperature control. The feed supply system to the anode consists in a nitrogen pressurized stainless steel tank of 2 L containing the methanol aqueous solution. This tank is large enough in order to prevent the excessive variation in methanol concentration during one-day experiment (less than 5%). A gear pump, computer controlled, is used to feed the methanol aqueous solution to the fuel cell. The storage tank is placed inside the oven for temperature control.

Regarding the feed to the cathode side, the required gas flow-rates are obtained using mass flow meters, controlled by a LabView based program. A stainless steel tank containing water is used to humidify the fuel cell gas feed streams at a controlled temperature. The feed cathode stream can then be bubbled through the heated water tank providing different humidity levels (at the fuel cell's operating temperature), as desired. The required feed pressure in the cell is controlled by a needle valve at the cathode exit.

The DMFC was fed with an aqueous 0.5M methanol solution (500 ml/min, 2.5 bar) to the anode side and humidified air (600 cm^3_N/min, 3 bar, 100% relative humidity) to the cathode side. MEAs characterization was performed measuring the DMFC current-voltage polarization curves at 90°C. The polarization curves were performed using a ElectroChem, Inc., CompuCell powerstation.

RESULTS AND DISCUSSION

The proton exchange membrane should provide a barrier for reactants to cross (methanol) while it should have high proton conductivity. However, a dried membrane shows usually a proton conductivity which is far lower than when it is hydrated. The pre-treatment of a MEA aims therefore to maximize the ability of the membrane to hydrate in order to increase its proton conductivity. To evaluate the pre-treatment effect on the membrane properties and DMFC performance, measurements of proton conductivity, permeability towards methanol and water and DMFC tests were carried out.

Proton Conductivity

From Fig. 2 it can be seen that the untreated sPEEK membranes, with and without inorganic modification, have considerably lower proton conductivity than that of Nafion®1135. Along with, and in agreement with previous published data (16), it can be observed that the incorporation of zirconium oxide in the sPEEK polymer matrix led to a composite membrane with lower conductivity compared to that of the pure polymer. On the other hand, from Fig. 2 it can also be seen that both sPEEK membranes were very sensitive, in terms of proton transport properties, to the pre-treatment. The proton conductivity increased by a factor of 6, while a less favorable effect was observed for Nafion®, whose proton conductivity increased by a factor of 1.3. Furthermore, it can be observed that the pre-treatment makes the proton conductivity of the pure sPEEK membrane even higher than that of Nafion®. We believe that the conductivity increase with the pre-treatment is due to improved water-assisted proton conductivity (broader water channels) (25). The proton conductivity

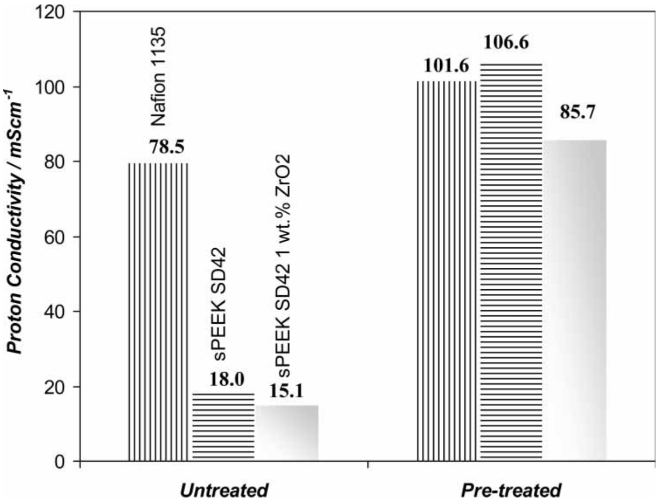

Figure 2. Proton conductivity in an acid electrolyte at 25°C of the studied membranes before and after the pre-treatment. Pre-treatment: 1 hour in boiling water (1 day before measurement).

of the pre-treated sPEEK membrane with 1 wt.% of zirconium oxide is the lowest of the pre-treated membranes, although the inorganic modification ensures a higher dimensional stability and, therefore, a higher long term use for DMFC purposes.

Water and Methanol Uptake

When the membrane is submitted to the pre-treatment some structural reorganization phenomena of the ionic clusters occurs, due to the membrane swelling. Therefore, experiments were carried out for a better understanding of the changes induced by the pre-treatment.

First of all, a set of measurements was performed to evaluate the membrane thickness change when it is submitted to the pre-treatment. In Table 1 is shown the increase of the membranes thickness with the pre-treatment applied, being the increase of the sPEEK-based materials particularly noteworthy. On the other hand, it should be mentioned that when a PEM is boiled in water a drastic structural reorganization occurs which allows a great increase on the volume fraction. This level of structural reorganization is not reached at the lower temperatures normally employed in DMFC operation. It was then decided to study the swelling behavior of the membrane at different temperatures below the water boiling point.

The weight increase of the studied membranes was measured after immersion in water, and methanol aqueous solution (1.5 and 6.0 M), at 40, 55 and 70°C. Results are given in Figs. 3a, 3b, and 3c, respectively. From these plots, it can be seen that swelling increases with temperature for all membranes studied, being the effect more noticeable for the plain sPEEK membrane and at the highest methanol concentration (6.0 M, Fig. 3c). From Fig. 3a and Fig. 3b, it can also be seen that at least up to 70°C for deionized water and 1.5M methanol aqueous solution, Nafion® 1135 has a higher swelling compared to that of the modified and unmodified sPEEK

Table 1. Membrane thicknesses before and after being pre-treated and corresponding percentage variation

Membrane	Pre-treatment	Thickness (μm)	Thickness variation (%)
sPEEK SD42	Not treated	42	43
	Pre-treated	60	
sPEEK SD42 1 wt.% ZrO_2	Not treated	50	40
	Pre-treated	70	
Nafion® 1135	Not treated	101	10
	Pre-treated	111	

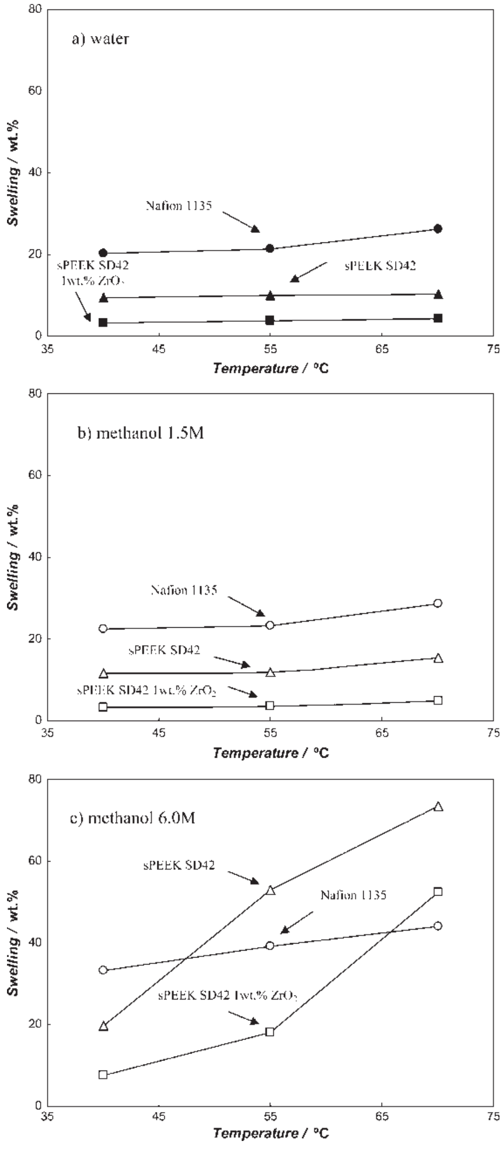

Figure 3. Membrane swelling in water (a), aqueous methanol 1.5 M solution (b) and aqueous methanol 6.0 M solution (c) as a function of temperature (batch experiments) for untreated membranes.

membrane. This trend is not verified for the 6.0 M aqueous methanol solution (Fig. 3c). At 55 and 70°C and for a 6.0 M methanol solution the pure sPEEK swells more than Nafion$^{®}$ 1135 (Fig. 3c). The same feature can be observed for the membrane with ZrO_2 at 70°C. This temperature and methanol concentration dependence of the swelling can be understood by taking into account the structural difference of Nafion® and sPEEK. Nafion® has a very hydrophobic and highly crystalline polymer matrix with ionic clusters attached to flexible side chains. This structure favors the formation of relatively large ionic clusters, separated from the matrix, where water and methanol can be easily sorbed. The swelled domains are then able to build a percolated channel structure, which is very favorable for water and methanol transport through the membrane. The highly crystalline matrix avoids an excessive dimensional change of the membrane as a whole, at least up to its melt temperature (>140°C) (26), which is far above the temperature range investigated here. Therefore, Nafion® swelling is less temperature and methanol concentration dependent. On the other hand, PEEK has sulfonic groups statistically distributed in a rigid aromatic backbone. When immersed in water/methanol, the membrane swells with reorganization of the ionic clusters structure, this structural reorganization being influenced by the sulfonation level, temperature and methanol concentration. When the temperature or methanol concentration increase, the amount of sorbed water/methanol allow the clusters to grow and to become well connected to each other. However, the clusters are not well separated from the matrix like in the case of Nafion® and water and methanol are much better distributed over the membrane. The absence of a highly crystalline matrix is responsible for an excessive swelling with undesired dimensional change of the membrane (27), which is particularly evident at higher temperatures. As mentioned before, the results obtained for the modified membrane indicate that the incorporation of zirconium oxide leads to the improvement of stability in terms of swelling.

The water uptake of the membrane (both for Nafion and sPEEK) is detrimental for the performance of the fuel cell if in excess, but it is essential for increasing the proton mobility, as inferred from the data presented in Fig. 2.

Permeability Towards Water and Methanol

Figures 4a and 4b plot the membrane's methanol permeability as a function of the temperature, for the untreated and pre-treated membranes, respectively. The values of the methanol permeability were normalized by the value obtained for the pre-treated Nafion 1135 at 70°C (4.07×10^{-5} mol s^{-1} m^{-1}). Nafion permeabilities obtained by us are in the same order of magnitude of those obtained by Dimitrova et al. (28) for Nafion 117 at 65°C. It can be seen that the methanol permeability increases with temperature. It can also be seen that Nafion® permeability towards methanol was always much higher than for both sPEEK membranes. As mentioned before, Nafion has well-formed and relatively wide ionic channels, while in the case of sPEEK the separation of the ionic clusters from the more hydrophobic matrix is

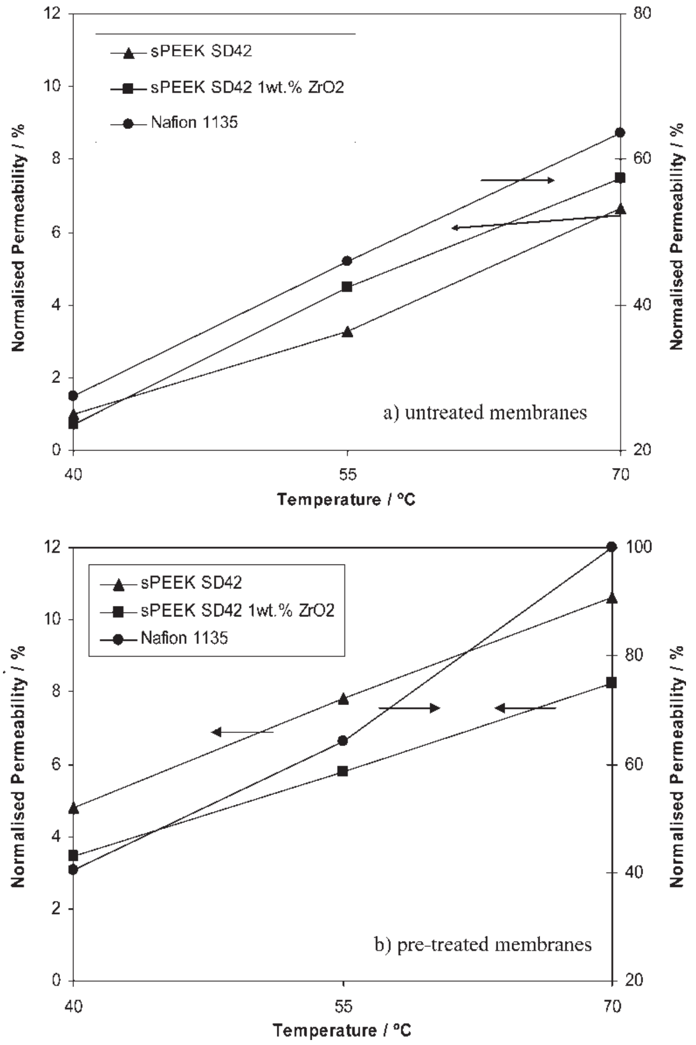

Figure 4. Permeability towards methanol obtained from pervaporation experiments of the studied untreated (a) and pre-treated (b) membranes as a function of temperature (pervaporation experiments with 6.0 M methanol aqueous solution). The permeability towards methanol is normalized by the permeability of the pre-treated Nafion 1135 at 70°C.

much less evident. Only smaller domains, which lead to relatively small channels, are present in a hydrated sPEEK membrane. Therefore, the methanol and water permeabilities are correspondently smaller. Along with Figs. 4a and 4b clearly show that the pre-treatment leads to an increase of the methanol permeability. This can be explained as a result of the broadening

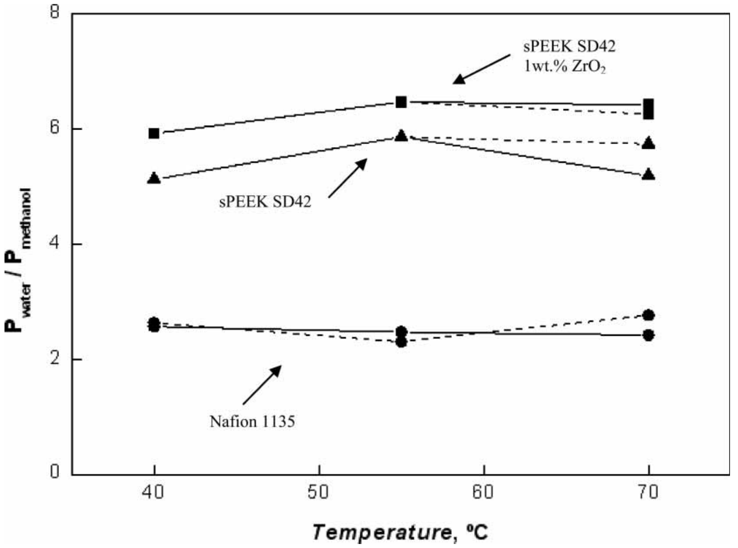

Figure 5. Water/methanol selectivity of the studied membranes as a function of temperature. Guide lines: (solid): untreated, (dash): pre-treated in boiling water for 1 hour (1 day before measurement).

of the ionic channels. In terms of both plain and inorganically modified sPEEK membranes, the incorporation of zirconium oxide leads, within the experimental uncertainty, to lower permeability coefficients.

The water/methanol selectivity as a function of the temperature is depicted in Fig. 5. A higher water/methanol selectivity means that for the same total flux, the amount of methanol crossover is smaller and, therefore, there will be lower methanol parasitic losses under DMFC operation. This plot shows that, as a general trend, the water/methanol selectivity changes only slightly with the temperature for pre-treated and untreated membranes. It also shows that the modified and unmodified sPEEK present higher selectivities when compared with Nafion®. Furthermore, it can be observed that the zirconium oxide incorporation leads to an increase in the water/methanol selectivity. In terms of both plain and composite sPEEK membranes, the pre-treatment effect in the selectivity is very small. A similar trend can be found for Nafion®.

DMFC Tests

In the previous sections the pre-treatment effect on the membrane proton conductivity and mass transport properties was studied. It is now important to characterize the membrane pre-treatment effect on the DMFC performance.

Table 2. Parasitic current density due to the methanol crossover through the pre-treated proton exchange membranes at 50 mV and 90°C

Membrane	Parasitic current density (mA · cm^{-2})
sPEEK SD42	61.1
sPEEK SD42 1wt.% ZrO_2	58.2
Nafion® 1135	66.8

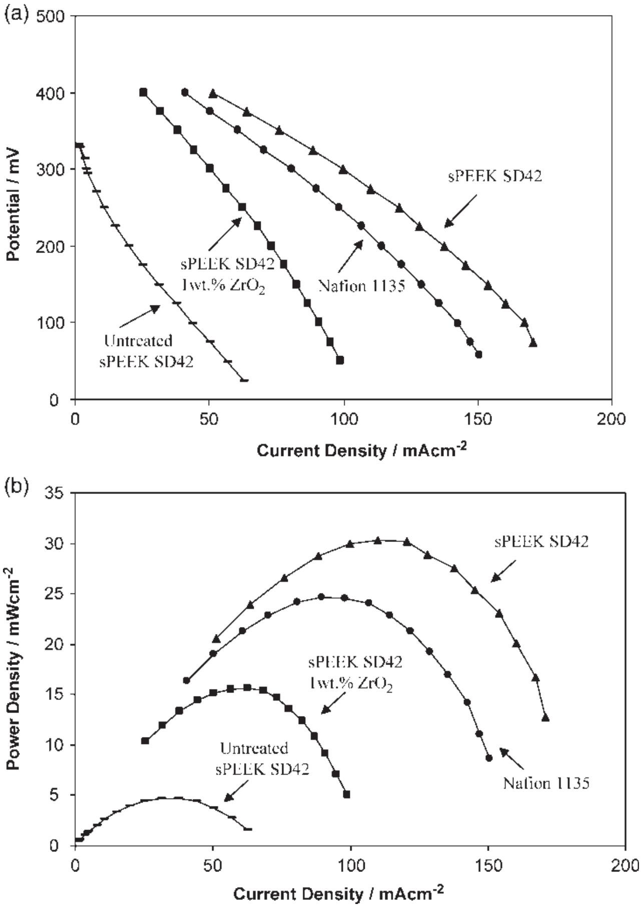

Figure 6. DMFC current density-voltage (a) and current density-power density (b) plots for all the pre-treated membranes and for the untreated sPEEK (SD = 42%) membrane at 90°C.

Although the permeability tests have been carried using a much more concentrated methanol solution (6.0 M) than employed in the DMFC tests (0.5 M), the permeability trends should be the same for both concentrations. Electrochemical characterization data concerning the methanol crossover are given in Table 2. Data are in agreement with Fig. 4b, confirming that Nafion® is the membrane more affected by the methanol crossover phenomena followed by the sPEEK membrane. Once again, the composite sPEEK membrane presents the better methanol barrier properties.

The DMFC current density-voltage and current density-power density plots, at 90°C, obtained using the pre-treated PEMs and untreated plain sPEEK membrane are shown in Figs. 6a and 6b, respectively. It can be seen that the plain sPEEK membrane pre-treatment leads to a dramatic increase in the achieved maximum power density output, from 4.72 mW/cm^2 (at 31.44 mA/cm^2) to 30.28 mW/cm^2 (at 110.15 mA/cm^2), Fig. 6b, which is 6.4 times higher. This increase can be ascribed to the higher degree of hydration attained by the membrane when submitted to the pre-treatment considered, which proton conductivity increases as much as the power density (Fig. 2). On other hand, it can also be seen that pre-treated Nafion and modified sPEEK membranes have a lower performance when compared to the pre-treated plain sPEEK membrane (Figs. 6a and 6b). As reported before, after treating the membranes their water channels become broader and the ionic clusters larger, both increasing the membrane proton conductivity (lower ohmic losses). This feature seems to indicate that the proton conductivity is the main effect behind the MEA performance under DMFC operation (29).

During the pre-treatment of the membranes there are morphological and structural changes that act directly on properties such as proton conductivity, permeability towards methanol and water, leading to increased DMFC performances. On the other hand, the pre-treatment was more effective on the plain sPEEK membrane than on Nafion®. Finally, the crucial role that the employed membrane pre-treatment plays in the MEA activation should be emphasized, being at the same time effective, quick and easy to perform.

CONCLUSIONS

In order to perform a critical analysis of the membrane pre-treatment effect on the membrane properties and MEA performance under DMFC operation, proton exchange membranes have been prepared using plain sPEEK ($SD = 42\%$) and modified sPEEK with 1.0 wt.% zirconium oxide incorporation, and then compared to Nafion® 1135. The membranes were pre-treated in boiling water during one hour, one day before operation. Proton conductivity and permeability towards methanol and water were evaluated by standard characterization methods using both pre-treated and untreated membranes.

Swelling experiments using water and methanol aqueous solutions (1.5 and 6.0 M concentration) were also performed in order to evaluate the effect of the temperature and methanol concentration on the membranes swelling.

The proton conductivity of the pre-treated membranes showed a significant increase compared to that of the untreated membranes. The effect is more pronounced for the sPEEK polymers, with the conductivity increasing by a factor of about 6, while the Nafion® membrane displayed only a 1.3 times increase.

On the other hand, the pervaporation experiments at 40, 55, and 70°C showed that the permeability coefficients of both water and methanol also increase with the pre-treatment. However, it was observed that the methanol/water selectivity remains unaffected. Nafion® showed higher swelling compared to sPEEK membranes only at 40°C.

The pre-treated and untreated plain sPEEK membranes were used in a DMFC and the current density-voltage curves investigated. It was observed that the pre-treatment of the plain sPEEK membrane enabled a dramatic improvement of the DMFC performance, leading to an increase of the maximum specific power from 4.72 mW/cm^2 (at 31.44 mA/cm^2) to 30.28 mW/cm^2 (at 110.15 mA/cm^2). Methanol crossover experiments are in line with the pervaporation tests. After the pre-treatment, the plain sPEEK membrane presents the best DMFC performance when compared with the Nafion® and modified sPEEK membranes. This increase in the membrane performance can be ascribed to the higher degree of hydration attained by the membrane when submitted to the pre-treatment, also indicating that the proton conductivity plays the major role behind the DMFC performance. Apparently, the pre-treated membranes show broader channels and larger ionic (sulfonic) clusters that allow it, after hydration, to perform much better than the untreated membranes.

ACKNOWLEDGEMENTS

The work of Vasco Silva, Valter Silva and Hugo Silva was supported by FCT (Grants SFRH/BD/6818/2001, SFRH/BD/18159/2004 and SFRH/3029/2000, respectively). Vasco Silva would like to acknowledge both FCT and GKSS for the grant assigned to him for his stay at GKSS Forschungszentrum GmbH. The present work was partially supported by FCT projects POCTI/EQU/38075/2001 and POCTI/EQU/45225/2002.

REFERENCES

1. Silva, V.S., Mendes, A., Madeira, L.M., and Nunes, S.P. (2005) Membranes for direct methanol fuel cell applications: analysis based on characterization, experimentation and modelling. *Advances in Fuel Cells*; Xiang-Wu Zhang (ed.); Research Signpost, 57.

2. Arico, A.S., Srinivasan, S., and Antonucci, V. (2001) DMFCs: From fundamental aspects to technology development. *Fuel Cells*, 1 (2): 133.
3. Yang, C., Srinivasan, S., Arico, A.S., Creti, P., Baglio, V., and Antonucci, V. (2001) Composite nafion/zirconium phosphate membranes for direct methanol fuel cell operation at high temperature. *Electrochem. Solid State Lett.*, 4 (1): A31.
4. Wasmus, S. and Kluver, A. (1999) Methanol oxidation and direct methanol fuel cells: a selective review. *J. Electroanal. Chemistry*, 461: 150.
5. Wang, J.-T., Wasmus, S., and Savinell, R.F. (1996) Real-time mass spectrometric study of the methanol crossover in a direct methanol fuel cell. *J. Electrochem. Soc.*, 143: 1239.
6. Kordesch, K. and Simader, G. (1996) *Fuel cells and their Applications*; VCH: Weinheim.
7. Bauer, B., Jones, D.J., Roziere, J., Tchicaya, L., Alberti, G., Casciola, M., Massinelli, I., Peraio, A., Besse, S., and Ramunni, E. (2000) Electrochemical characterisation of sulfonated polyetherketone membranes. *J. New Mater. Electrochem. Systems*, 3 (1): 93.
8. Zaidi, S.M.J., Mikailenko, S.D., Robertson, G.P., Guiver, M.D., and Kaliaguine, S. (2000) Proton conducting composite membranes for polyether ether ketone and heteropolyacids for fuel cell applications. *J. Membr. Sci.*, 173 (1): 17.
9. Mikhailenko, S.D., Zaidi, S.M.J., and Kaliaguine, S. (2001) Sulfonated polyether ether ketone composite polymer electrolyte membranes. *Catal. Today*, 67 (1–3): 225.
10. Kreuer, K.A. (2001) On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J. Membr. Sci.*, 185 (1): 3.
11. Kerres, J., Zhang, W., Jörissen, L., and Gogel, V. (2002) Application of different types of polyaryl-blend-membranes in DMFC. *J. New Mater. Electrochem. Systems*, 5: 97.
12. Alberti, G., Casciola, M., Massinelli, L., and Bauer, B. (2001) Polymeric proton conducting membranes for medium temperature fuel cells (110–160°C). *J. Membr. Sci.*, 185 (1): 73.
13. Silva, V., Ruffmann, B., Silva, H., Mendes, A., Madeira, M., and Nunes, S. (2004) Zirconium oxide modified sulfonated poly(ether ether ketone) membranes for direct methanol fuel cell applications. *Mater. Sci. Forum.*, 455: 587.
14. Ponce, M.L., Prado, L., Ruffmann, B., Richau, K., Mohr, R., and Nunes, S.P. (2003) Reduction of methanol permeability in polyetherketone-heteropolyacid membranes. *J. Membr. Sci.*, 217 (1): 5.
15. Manea, C. and Mulder, M. (2002) Characterization of polymer blends of polyethersulfone/sulfonated polysulfone and polyethersulfone/sulfonated polyetheretherketone for direct methanol fuel cell applications. *J. Membr. Sci.*, 206 (1–2): 443.
16. Silva, V.S., Ruffmann, B., Silva, H., Gallego, Y.A., Mendes, A., Madeira, L.M., and Nunes, S.P. (2005) Proton electrolyte membrane properties and direct methanol fuel cell performance. I. Characterization of hybrid sulfonated poly(ether ether ketone)/zirconium oxide membranes. *J. Power Sources*, 140 (1): 34.
17. Kho, B.-K., Oh, I.-H., Hong, S.-A., and Ha, H.Y. (2004) The effect of pretreatment methods on the performance of passive DMFCs. *Electrochimica Acta.*, 50 (2–3): 781.
18. Kim, J., Lee, H., Hong, S., and Ha, H.Y. (2005) Impedance analysis on transient behavior of DMFC anodes during preconditioning process. *J. Electrochem. Soc.*, 152 (12): A 2345.

19. Xu, Z., Qi, Z., and Kaufman, A. (2003) Modification and improvement of proton-exchange membrane fuel cells via treatment using peracetic acid. *J. Power Sources*, 115 (1): 49.
20. Jia, N.Y., Martin, R.B., Qi, Z.G., Lefebvre, M.C., and Pickup, P.G. (2001) Modification of carbon supported catalysts to improve performance in gas diffusion electrodes. *Electrochimica Acta.*, 46 (18): 2863.
21. Qi, Z. and Kaufman, A. (2002) Activation of low temperature PEM fuel cells. *J. Power Sources*, 111 (1): 181.
22. Rozière, J. and Jones, D.J. (2003) Non-fluorinated polymer materials for proton exchange membrane fuel cells. *Annu. Rev. Mater. Res.*, 33: 503.
23. Huang, R.Y.M., Shao, P.H., Burns, C.M., and Feng, X. (2001) Sulfonation of poly(ether ether ketone) (PEEK): kinetic study and characterization. *J. Appl. Polym. Sci.*, 82 (11): 2651.
24. Silva, V.S., Ruffmann, B., Silva, H., Silva, V.B., Mendes, A., Madeira, L.M., and Nunes, S.P. (2006) Zirconium oxide hybrid membranes for direct methanol fuel cells — Evaluation of transport properties. *J. Membr. Sci.*, 284 (1–2): 137.
25. Kreuer, K.D. (2001) On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J. Membr. Sci.*, 185 (1): 29.
26. Yang, B. and Manthiram, A. (2006) Comparison of the small angle X-ray scattering study of sulfonated poly(etheretherketone) and Nafion membranes for direct methanol fuel cells. *J. Power Sources*, 153 (1): 29.
27. Yang, B. and Manthiram, A. (2003) Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cells. *Electrochem. Solid State Lett.*, 6: 229.
28. Dimitrova, P., Friedrich, K.A., Stimming, U., and Vogt, B. (2002) Modified Nafion–based membranes for use in direct methanol fuel cells. *Solid State Ionics.*, 150 (1–2): 115.
29. Silva, V.S., Mendes, A., Madeira, L.M., and Nunes, S.P. (2006) Proton exchange membranes for direct methanol fuel cells: Properties critical study concerning methanol crossover and proton conductivity. *J. Membr. Sci.*, 276 (1–2): 126.