Mass transport of direct methanol fuel cell species in sulfonated poly(ether ether ketone) membranes

V.S. Silva a, B. Ruffmann a, S. Vetter a, M. Boaventura b, A.M. Mendes b,∗, L.M. Madeira b, S.P. Nunes a

a GKSS Research Centre, Max-Planck Str., 21502 Geesthacht, Germany
b LEPAE, Chemical Engineering Department, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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Abstract

Homogeneous membranes based on sulfonated poly(ether ether ketone) (sPEEK) with different sulfonation degrees (SD) were prepared and characterized. In order to perform a critical analysis of the SD effect on the polymer barrier and mass transport properties towards direct methanol fuel cell species, proton conductivity, water/methanol pervaporation and nitrogen/oxygen/carbon dioxide pressure rise method experiments are proposed. This procedure allows the evaluation of the individual permeability coefficients in hydrated sPEEK membranes with different sulfonation degrees. Nafion® 112 was used as reference material. DMFC tests were also performed at 50°C. It was observed that the proton conductivity and the permeability towards water, methanol, oxygen and carbon dioxide increase with the sPEEK sulfonation degree. In contrast, the SD seems to not affect the nitrogen permeability coefficient. In terms of selectivity, it was observed that the carbon dioxide/oxygen selectivity increases with the sPEEK SD. In contrast, the nitrogen/oxygen selectivity decreases. In terms of barrier properties for preventing the DMFC reactants loss, the polymer electrolyte membrane based on the sulfonated poly(ether ether ketone) with SD lower or equal to 71%, although having slightly lower proton conductivity, presented much better characteristics for fuel cell applications compared with the well known Nafion® 112. In terms of the DMFC tests of the studied membranes at low temperature, the sPEEK membrane with SD = 71% showed to have similar performance, or even better, as that of Nafion® 112. However, the highest DMFC overall efficiency was achieved using sPEEK membrane with SD = 52%.

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1. Introduction

At present the direct liquid methanol fuel cell (DMFC) is one of the most promising power supply candidates for portable electric devices [1–3]. Methanol has the advantage as energy carrier of having a significant electroactivity and being easily oxidized directly to water and carbon dioxide in catalyst alloys. Apart from that, it is easy to handle and transport (liquid at room temperature), is used in low concentrations in the DMFC (typically 2%) and is less dangerous than hydrogen. Furthermore, it can be produced from a variety of sources (natural gas, coal, wood) and is biodegradable [2].

One of the main obstacles for the development of the DMFC is that usually it employs the same proton exchange membranes that are used in the hydrogen fuel cell [3]. The most common are the perfluorinated ion-exchange polymers, such as Nafion® from Dupont (Fig. 1) or Nafion-like polymers supplied by Dow, Asahi and some other companies. This kind of membranes combines the extremely high hydrophobicity of the perfluorinated backbone with the extremely high hydrophilicity of the sulfonic acid functional groups [4]. In the presence of water, this effect is even more pronounced due to the aggregation of the hydrophilic domains (nanoseparation) [4]. Consequently, methanol and water are readily transported across perfluor sulfonic acid membranes [1,5,6]. Methanol crossover from the anode to the cathode is detrimental to DMFC performance as it reduces the Coulombic efficiency and cell voltage, leading to an efficiency reduction down to 35% [6]. On the other hand, the high water permeability in perfluorinated membranes can cause
cathode flooding and thus, lower cathode performance [5]. The loss of oxygen from the cathode to the anode is also detrimental for the DMFC efficiency, although it can be neglected in comparison with the effect of the methanol crossover. Nitrogen and carbon dioxide mass transfer in the proton exchange membrane does not affect significantly the DMFC performance. However, the knowledge of the membrane permeability towards DMFC species can be useful for theoretical modeling purposes, enabling the calculation of their total concentration profiles in the fuel cell. Furthermore, it can be also helpful for evaluating the fuel cell total efficiency, where the knowledge of the carbon dioxide mass balance (with CO2 resulting from methanol crossover) enables the calculation of their concentration profiles in the fuel cell. Apart from that, the sPEEK polymer allows direct casting from organic solutions, which is by far a less expensive process compared to the manufacturing of perfluorosulfonic membranes. However, having a weaker hydrophobic domain, the sPEEK polymer is less morphologically stable [11].

The present work focuses on the evaluation of the permeability coefficients and mass transport properties of DMFC species in sulfonated poly(aryl ether ketone) polymer with different sulfonation degrees. In this study the proton conductivity was obtained via impedance spectroscopy, using sulfuric acid 0.33 M as electrolyte. The permeabilities towards water and methanol were evaluated by pervaporation experiments. On the other hand, nitrogen, oxygen and carbon dioxide permeability coefficients were obtained by a pressure rise method in presence of water vapour (swollen membrane). Apart from this, the studied membranes were also tested in real DMFC experiments, and the corresponding polarizations curves obtained. It was also performed a prediction of the fuel cell efficiency for each studied membrane, using the evaluation method as described in Ref. [12]. Nafion® 112 was used as reference material.

2. Experimental

2.1. Materials and methods

sPEEK polymers with sulfonation degrees of 47, 52, 71 and 78% were prepared following the procedure described in Ref. [13]. Poly(aryl ether ketone) was supplied as pellets by Victrex. The sulfonation degree was determined by elemental analysis and by H NMR. Commercially available Nafion® 112 was purchased from Aldrich.

2.2. Membrane preparation

Sulfonated poly(aryl ether ketone) polymers were dissolved in dimethylsulfoxide (6%, w/w) and left to stir for 1 day. The sPEEK polymers with lower sulfonation degrees (SD = 47 and 52%) were dissolved increasing the temperature to 50–70 °C, while the others were dissolved at room temperature. After filtration, the final solutions were cast in a hydrophobised glass plate heated to 70 °C. The thickness of the prepared membranes with sulfonation degrees of 47, 52, 71 and 78% were 87, 55, 52 and 59 μm, respectively.

2.3. Characterization methods

2.3.1. Proton conductivity

Conductivity measurements were carried out at 25 °C in the cell described in Ref. [14], using ac impedance spectroscopy. A membrane sample was placed in a liquid electrolyte solution
(0.33 M H₂SO₄) between two platinum electrodes, which have a diameter of 2.8 cm and a distance between them of about 2 mm. The minimum phase angle impedance corresponding to the system membrane/electrolyte was measured after 18 h of stabilization. As pretreatment, samples were immersed in water at room temperature during 3 days to ensure total leaching. One hour before the measurement, the samples were immersed for 1 h in 0.33 M H₂SO₄. The spectrometer used was a HP 4284A working in the frequency range between 100 and 10⁷ Hz.

2.5.2. Liquid permeability measurements
Permeabilities towards water and methanol were evaluated through pervaporation experiments at 25 °C with a 20 wt.% methanol aqueous solution. The pervaporation set-up is described elsewhere [15]. Prior to all measurements, samples were immersed in the feed solution at room temperature for 1 h.

The performance of a pervaporation process can be described by the flux through the membrane and the separation factor [16]. Assuming ideal mixing in the feed and permeate sides, the mass transfer during liquid permeation can be divided into three consecutive steps [17]:

- Selective sorption of molecules into the membrane at the feed side.
- Selective diffusion through the membrane.
- Selective desorption into the vapour phase at the permeate side.

According to Binning et al. [18], in the pervaporation process the selective diffusion through the membrane is the slowest step and, therefore, it can be assumed that the mass transfer of species through the membrane is practically not affected by sorption and desorption steps. Thus, the species' permeability coefficients in pervaporation processes can be obtained from the sorption–diffusion model stated by Lee [20], assuming that sorption is well described by Henry's law [21] and steady-state sorption–diffusion model formed by Lonsdale et al. for the transport in pervaporation processes can be obtained from the solution–desorption steps. Thus, the species' permeability coefficients and, therefore, it can be assumed that the mass transfer of species selective diffusion through the membrane is the slowest step.

2.3.3. Gas permeability measurements
Nitrogen, oxygen and carbon dioxide permeability coefficients were evaluated at 20 °C using the pressure rise method [23]. The permeation measurements were carried as described by Dvoriš et al. [23]. The gas feed was previously humidified (100% relative humidity) 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.

2.4. DMFC tests
The membrane electrode assemblies (MEAs) were prepared by hot pressing the membrane samples between two Etec® ELAT electrodes. Supported PtRu (0.5 mg/cm² 20 wt.% PtRu (1:1) on carbon with 0.6–0.8 mg/cm² Nafion®/PTFE) and Pt (0.5 mg/cm² 30 wt.% Pt on carbon with 0.6–0.8 mg/cm² Nafion®/PTFE) were used as anode and cathode electrodes, respectively. The membranes were conditioned in boiling water for 1 h and then pressed with the electrodes at 80 °C and 74 bar for 2 min. The DMFC experimental set-up is described elsewhere [24]. The DMFC with the prepared MEAs (25 cm²) was operated with an aqueous 0.5 M methanol solution (26 ml/min, 2.5 bar) on the anode side and humidified air (600 sccm/min, 3 bar, 100% relative humidity) on the cathode side. The temperature of the cell was maintained at 50 °C. The MEAs' characterization was performed measuring the DMFC current–voltage polarization curves and the CO₂ concentration in the cathode outlet at constant voltage current (CV: 50 mV) and open circuit voltage (OCV). The CO₂ concentration in the cathode outlet was monitored as a measure of the methanol crossover during DMFC operation [25]. The potential, Faraday and overall DMFC efficiencies were evaluated as described in Ref. [12]. The Faraday efficiency is defined as the ratio of the converted fuel for current production (anode) to the total amount of converted fuel (anode and cathode). On the other hand, the potential efficiency is defined as the voltage loss of the DMFC compared to the standard cell voltage due to the overall potential losses. Finally, the overall DMFC efficiency is the combination of both Faraday and potential efficiencies.

3. Results and discussion
3.1. Proton conductivity
It is known that the main function of a polymer electrolyte membrane in the DMFC is to conduct protons from the anode...
to the cathode, while preventing the reactants loss. The effect of
the sPEEK sulfonation degree on the conductivity of the studied
membranes is shown in Fig. 3. As expected, the proton con-
ductivity increases with the sulfonation degree of the sPEEK
polymer. As a consequence of the higher number of sulfonated
sites (Fig. 2), the amount of sorbed water by the polymer is
higher, leading to the formation of water-mediated pathways for
protons. On the other hand, the proton conductivity measured
for Nafion® 112 at 25 °C was 88.6 mS cm\(^{-1}\) (Table 1), which
is approximately 18% higher than that of the sPEEK polymer
with the highest sulfonation degree studied (SD = 78%). This
fact can be explained based on the distinct transport proper-
ties due to morphological aspects [4]. As mentioned before, due
to the smaller hydrophilic/hydrophobic difference, the hydrated
sulfonated poly(ether ether ketone) has narrower and less sepa-
rated water channels compared to those of Nafion [4]. Therefore,
for the sPEEK polymer a smaller water dynamic assisted proton
conductance is expected. In order to reach higher conductivi-
ties, the sulfonation degree of the sPEEK polymer should be
increased, but the mechanical and chemical properties will tend
also to progressively deteriorate.

3.2. Permeability towards water and methanol

Transport of water and methanol in polymer electrolyte mem-
branes depends on the complex interactions between permeates
and the polymeric membrane matrix [26]. In sPEEK membranes,
number of sulfonic groups should lead to an increase in the selectivity towards water/methanol because water is preferentially transported in the ionic moieties [26]. However, due to the high molecular interaction between methanol and water, the sulfonation degree seems to not affect the selectivity. It can be assumed that the hydrogen-bonding interaction between water and methanol competes with the sulfonic acid groups assisted mass transfer. In the particular case of the sPEEK membrane with SD = 78%, the selectivity decreases to the lowest level. This can be explained by the excessive swelling of the membrane due to the high sulfonation degree.

In comparison to Nafion® 112 (Table 1), the sPEEK polymer is always more selective towards water/methanol. As before, this fact can be explained by the previously mentioned distinct transport properties [4]. Due to the sPEEK narrower and less separated water channels compared to those of Nafion® [4], higher electrostatic interactions between water/methanol and –SO\(_3\)H groups occurs. Therefore, the hydrogen-bonding interactions between water and methanol will probably be higher for Nafion® in comparison with those of sPEEK, decreasing its selectivity towards water permeation.

3.3. Permeability towards nitrogen, oxygen and carbon dioxide

Transport phenomenon involved in the permeation of nitrogen, oxygen and carbon dioxide in the swollen polymer electrolyte membrane depends on the interactions between permeates with the polymeric membrane matrix and sorbed water. Depending on the sulfonation degree, the polymer will have a certain degree of swelling and, therefore, the amount of sorbed water will influence the gas permeation. The nature of the polymer is also important due to the acidity associated with the sulfonic groups.

The computed nitrogen, oxygen and carbon dioxide permeability coefficients are given in Fig. 6. It shows that the oxygen and carbon dioxide permeability coefficients increase with the sPEEK sulfonation degree. In contrast, it can be noticed that the membrane permeability to nitrogen is almost not affected. For low sulfonation degrees the permeability towards oxygen is almost the same as the one for nitrogen. Apart from that, for all sulfonation degrees the permeability towards carbon dioxide is much higher compared with that of the other gases.

In Table 2 are given the values obtained in the present study for Nafion® 112 with respect to gas permeation. It can be seen that the permeabilities are more than an order of magnitude higher than those obtained for sPEEK polymer (Fig. 6). As mentioned previously, these high permeation ratios can be explained by the wider and more separated water filled channels of Nafion compared with the sPEEK polymer. This difference in permeabilities is much significant than that recorded for methanol and water (cf. Table 1 and Fig. 4). However, the operation conditions of the pervaporation – to obtain the permeabilities towards methanol and water – and gas permeation experiments are quite different. The fact of using methanol in the pervaporation experiments should increase the swelling of the sPEEK membranes above the Nafion [27]. This trend is more noticed for the sPEEK polymer with higher sulfonation degree (excessive swelling and, consequently, wider water filled channels). This explains the similar sPEEK permeability towards water and methanol in comparison to Nafion. In contrast, for gas permeation experiments, the samples are only in contact with water at 20 °C. Therefore, even for higher SD, no excessive swelling is expected and therefore the water filled channels dimensions remain distinct from the ones of Nafion.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Nafion® 112</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{\text{CO}_2} ) (Barrer)</td>
<td>110.18</td>
</tr>
<tr>
<td>( P_{\text{O}_2} ) (Barrer)</td>
<td>3.39</td>
</tr>
<tr>
<td>( P_{\text{N}_2} ) (Barrer)</td>
<td>6.48</td>
</tr>
<tr>
<td>( P_{\text{N}<em>2}/P</em>{\text{O}_2} )</td>
<td>0.40</td>
</tr>
<tr>
<td>( P_{\text{CO}<em>2}/P</em>{\text{O}_2} )</td>
<td>12.99</td>
</tr>
</tbody>
</table>
Fig. 7. Selectivity towards N$_2$/O$_2$ and CO$_2$/O$_2$ of sPEEK membranes as a function of the sulfonation degree (pressure rise experiments at 20$^\circ$C).

Fig. 7 shows that the nitrogen/oxygen selectivity decreases with the sPEEK sulfonation degree. In terms of Nafion selectivity for gases permeation (Table 2), it can be seen that the nitrogen/oxygen selectivity has the same order of magnitude as the one calculated for sPEEK polymer. According to the theory of the narrower water filled channels in the swollen sPEEK membrane and, consequently, larger contact surface between the molecules of dissolved gas and the hydrophobic/hydrophilic interface [4], the acid behavior of carbon dioxide and its possible interaction with the –SO$_3$H groups can be suggested as the reason for the higher selectivity towards carbon dioxide in comparison with Nafion®. Thus, in the case of carbon dioxide it can be assumed that the mass transport is firstly governed by the solubility/diffusion of the gas in the sorbed water contained in the polymer channels and, secondly, by the interaction with the acid sulfonic groups. In contrast, for oxygen and nitrogen the mass transport is governed mostly by the solubility/diffusion in the water sorbed in the polymer channels because the wider/narrower channels seems to not affect the mass transport.

3.4. DMFC tests

The current density–voltage and current density–power density plots of MEAs obtained from sPEEK membranes with SD = 52 and 71% at 50$^\circ$C are shown in Fig. 8. The curves corresponding to the membrane with SD = 47% are not presented because this membrane showed high resistance at the test temperature. On the other hand, the plots corresponding to the sPEEK membrane with SD = 78% are not presented because this membrane is not stable for DMFC applications at 50$^\circ$C. Even so, the results can be used for comparison of the tested membranes with Nafion® 112. The maximum power output achieved for this membrane was 1.19 mW/cm$^2$ at 8.67 mA/cm$^2$, in comparison with 1.16 mW/cm$^2$ at 6.88 mA/cm$^2$ for Nafion® 112. Apart from this, from the plots presented in Fig. 8 it can be also seen that the open circuit voltage (null current density) increases with the decrease of the sPEEK SD. This fact can be explained by the lower methanol crossover (lower potential loss) due to the improved barriers properties of the membranes with lower SD (Fig. 4). In terms of Nafion® 112, it can be observed that the DMFC using this membrane presents the lowest open circuit voltage (OCV) of the studied membranes (high methanol permeability).

In Fig. 9, both DMFC potential and Faraday efficiencies are given for the selected membranes as a function of current density. From these plots it can be seen that the membrane with SD = 52% presents improved properties in terms of Faraday efficiency (improved fuel utilization). Furthermore, the DMFC using this membrane has the highest potential efficiency for open circuit voltage (null current density) but when current density...
always higher potential efficiency than that of Nafion® 112, it using sPEEK membrane with SD = 71%, although presenting

In order to study the mass transport of DMFC species, various sulfonated poly(ether ether ketone) membranes with different sulfonation degrees have been prepared and characterized. The mass transport mechanisms of these species were compared with those for Nafion® 112.

Impedance spectroscopy measurements at 25 °C using an acid electrolyte (H2SO4, 0.33 M) showed that the proton conductivity increases with the sulfonation degree of the sPEEK polymer. On the other hand, pervaporation experiments at 25 °C and 20 wt.% methanol feed showed that the the permeability coefficients of both water and methanol also increase with the sulfonation degree. It was observed that the sPEEK membranes with sulfonation degrees less than 71% have higher water/methanol selectivity and lower water and methanol fluxes compared to Nafion® 112. The sPEEK polymer with sulfonation degree of 78% provided high methanol and water fluxes and lower selectivity due to its lower morphological stability (excessive swelling). In terms of the membrane gas permeability towards nitrogen, oxygen and carbon dioxide in the presence of water vapour (100% r.h.), experimental results obtained by the pressure rise method, at 20 °C, showed that the permeability coefficients of carbon dioxide and oxygen increase with the sulfonation degree of the sPEEK polymer. The effect in the nitrogen permeability coefficient is mostly negligible. It was also found that the carbon dioxide/oxygen selectivity increases with the sulfonation degree. The opposite trend is verified for nitrogen/oxygen selectivity. From the DMFC tests it was observed that the fuel cell performance increases with the sulfonation degree. The results showed that the DMFC using a sPEEK membrane with sulfonation degree of 71% achieves a better performance than when using Nafion® 112. Apart from this, from the polarization curves it could be noticed that the open circuit voltage (null current density) decreases with the sPEEK SD (higher methanol crossover). DMFC operation using sPEEK membranes with SD lower than 71% provided a higher open circuit voltage than that of Nafion® 112. It was also observed that the potential efficiency decreases with the sPEEK SD. On the other hand, it was found that the Faraday efficiency (fuel effective utilization) increases when decreasing the sPEEK SD. From the predicted overall DMFC efficiency using the studied membranes, it was observed that the maximum efficiency is achieved for the lowest sPEEK SD. Although achieving the highest DMFC performance when using sPEEK membranes with SD = 70%, the application of this membrane proved to be less efficient in the DMFC due to higher methanol crossover (lower Faraday efficiency).

Based on the criterion of the reactants loss minimization, chemical stability along with enough proton conductivity, the sPEEK membrane exhibits characteristics that can improve the DMFC performance and the global efficiency when compared to Nafion® 112.

4. Conclusions

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Acknowledgements
Appendix A. Nomenclature

A membrane area (m²)
J molar flow rate (mol s⁻¹)
\kappa proton conductivity (mS cm⁻¹)
p pressure (Pa)
P permeability coefficient (Barrer)
R ideal gas constant (J mol⁻¹ K⁻¹)
T temperature (K)
X molar fraction

Greek letters
\alpha overall selectivity
\delta thickness (m)
\gamma activity coefficient

Subscripts
i species i
j species j
L liquid phase
M membrane
V vapor phase

Superscript
sat equilibrium state

References