

Performance and efficiency of a DMFC using non-fluorinated composite membranes operating at low/medium temperatures

V.S. Silva^b, S. Weisshaar^c, R. Reissner^c, B. Ruffmann^a, S. Vetter^a, A. Mendes^{b,*},
L.M. Madeira^b, S. 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

^c Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Technische Thermodynamik, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

Accepted 21 December 2004

Available online 26 April 2005

Abstract

In order to increase the chemical/thermal stability of the sulfonated poly(ether ether ketone) (sPEEK) polymer for direct methanol fuel cell (DMFC) applications at medium temperatures (up to 130 °C), novel inorganic–organic composite membranes were prepared using sPEEK polymer as organic matrix (sulfonation degree, SD, of 42 and 68%) modified with zirconium phosphate (ZrPh) pretreated with *n*-propylamine and polybenzimidazole (PBI). The final compositions obtained were: 10.0 wt.% ZrPh and 5.6 wt.% PBI; 20.0 wt.% ZrPh and 11.2 wt.% PBI. These composite membranes were tested in DMFC at several temperatures by evaluating the current–voltage polarization curve, open circuit voltage (OCV) and constant voltage current (CV, 35 mV). The fuel cell ohmic resistance (null phase angle impedance, NPAI) and CO₂ concentration in the cathode outlet were also measured. A method is also proposed to evaluate the fuel cell Faraday and global efficiency considering the CH₃OH, CO₂, H₂O, O₂ and N₂ permeation through the proton exchange membrane (PEM) and parasitic oxidation of the crossover methanol in the cathode. In order to improve the analysis of the composite membrane properties, selected characterization results presented in [V.S. Silva, B. Ruffmann, S. Vetter, A. Mendes, L.M. Madeira, S.P. Nunes, Catal. Today, in press] were also used in the present study. The unmodified sPEEK membrane with SD = 42% (S42) was used as the reference material. In the present study, the composite membrane prepared with sPEEK SD = 68% and inorganic composition of 20.0 wt.% ZrPh and 11.2 wt.% PBI proved to have a good relationship between proton conductivity, aqueous methanol swelling and permeability. DMFC tests results for this membrane showed similar current density output and higher open circuit voltage compared to that of sPEEK with SD = 42%, but with much lower CO₂ concentration in the cathode outlet (thus higher global efficiency) and higher thermal/chemical stability. This membrane was also tested at 130 °C with pure oxygen (cathode inlet) and achieved a maximum power density of 50.1 mW cm⁻² at 250 mA cm⁻².

© 2005 Elsevier B.V. All rights reserved.

Keywords: Sulfonated poly(ether ether ketone); Composite membrane; Zirconium phosphate; Polybenzimidazole; Direct methanol fuel cell; Fuel cell characterization

1. Introduction

Direct methanol fuel cells (DMFCs) based on solid polymer electrolyte (SPE) are promising candidates for transport applications because they do not require any fuel processing equipment and can be operated at temperatures up to 140 °C

(Fig. 1) [2]. The main disadvantage of the DMFC system is the relative low power density compared to polymer electrolyte membrane fuel cells (PEMFC) operating on hydrogen [3].

The lower cell performance of a DMFC is caused mainly by the poor kinetics of the anode electro-oxidation of methanol and by the crossover of methanol through the polymer electrolyte membrane (PEM) [3]. The slow oxidation kinetic of methanol to carbon dioxide is due to the formation

* Corresponding author. Tel.: +351 22 508 1695; fax: +351 22 508 1449.

E-mail address: mendes@fe.up.pt (A. Mendes).

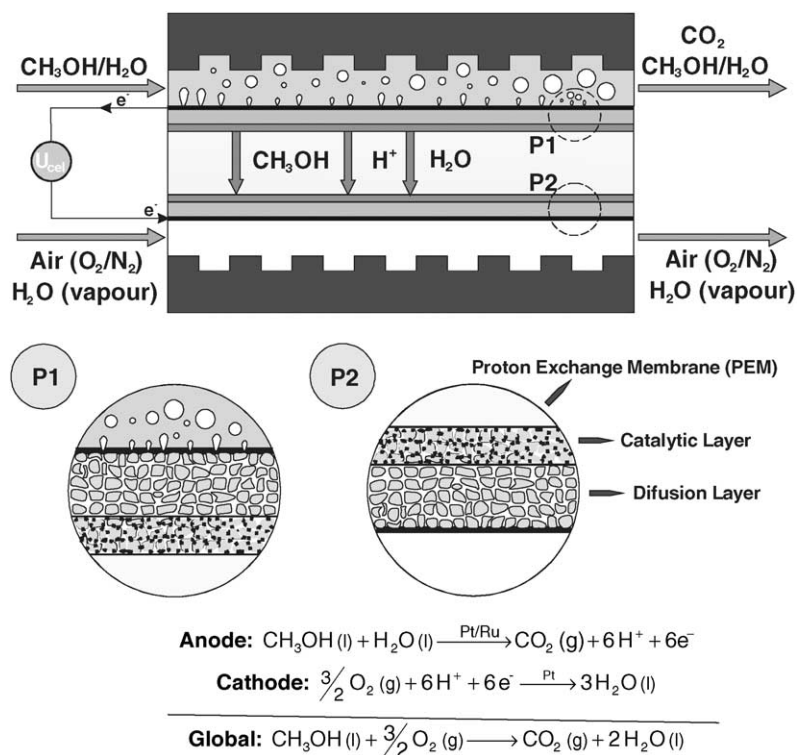


Fig. 1. Sketch of a DMFC: water, methanol and proton transport through the proton exchange membrane.

of carbon monoxide as an intermediate which strongly adsorbs on the Pt catalyst surface [4]. Since the adduct Pt–CO is thermolabile, the catalytic electro-oxidation activity towards methanol can be improved increasing the DMFC operation temperature to about 120–130 °C, in order to drastically reduce or eliminate the catalyst poisoning [4,5]. Apart from that, an increase in the operation temperature improves the oxygen reduction reaction at the cathode, the polymer electrolyte membrane proton conductivity and decreases the polarization effects [3,5–8]. However, the methanol crossover is believed to increase with temperature and becomes the prevailing effect, at least, for the perfluorinated membranes [6].

In general, DMFCs operating at medium temperatures require membranes that are thermally stable, proton conductive for distinct hydration conditions (vapour feed) and present good barrier properties towards the DMFC species, mainly methanol. Nowadays, the commercially available membrane electrode assemblies (MEAs) use plain perfluorosulfonic membranes, such as Nafion[®], that are thermally stable but not suitable for DMFC applications [3]. Apart from being costly, this type of membrane has high permeability towards methanol even at low temperatures, which drastically reduces the DMFC performance [9]. These limitations stimulated the development of alternative polymeric proton exchange membranes, such as sulfonated poly(ether ether ketone) (sPEEK) [10–13]. Recently, Li et al. reported better DMFC performances for sPEEK membranes with sulfonation degrees of 39 and 47% at 80 °C compared to Nafion[®] 115 [14]. In our laboratories, similar results were obtained for a sPEEK mem-

brane with SD = 42%, although this membrane was not mechanically stable when operated for longer periods than 4 days at 110 °C. It was observed that the membrane breaks and a strong leakage of gas from cathode to anode occurred.

Therefore, the present study aims to evaluate DMFC tests at low and medium temperatures (from 50 up to 130 °C) using non-fluorinated composite membranes prepared using sPEEK polymer as polymer matrix (SD = 42 and 68%), incorporating different amounts of α -zirconium phosphate (ZrPh) pretreated with *n*-propylamine and polybenzimidazole (PBI). In the present paper it is also described a method for the evaluation of the fuel cell efficiency.

2. Experimental

2.1. Materials and methods

sPEEK polymer with sulfonation degrees of 42 and 68% were obtained by sulfonation of poly(ether ether ketone) 450P, supplied as pellets by Victrex (Lancashire, UK), following the procedure described elsewhere [15]. The sulfonation degree was determined by elemental analysis and by H NMR as described by Nolte et al. [16].

2.2. Zirconium phosphate preparation

Layered α -zirconium phosphate (ZrPh) was synthesized using the method described by Ruffmann et al. [17], where

ZrOCl₂ is used as precursor of ZrO₂. In order to promote the exfoliation of the zirconium phosphate layers, the ZrPh solution (6 wt.% in dimethylformamide, DMF) was treated adding *n*-propylamine solution (1 M in DMF) using the weight ratio 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) was added and the dispersion further stirred for 6 days at the same temperature.

2.3. Membrane preparation

The sPEEK polymer was dissolved in dimethylsulfoxide (DMSO). Then the ZrPh/PBI dispersion solution was added and the final solution left to stir for 3 days at 60 °C. After filtration, the solution was cast on a glass plate heated at 70 °C. The glass plate was previously hydrophobized with octadecyl trichlorosilane. After casting, the membranes were stored in a vacuum oven for 24 h at 90 °C. The final thickness of the composite membranes varied between 63 and 84 μm [1]. It is expected that the membrane thickness should influence the measurements in the fuel cell giving a lower current for 35 mV, higher OCV, higher impedance and lower methanol permeation for a thicker membrane. However, in the present study it is assumed that the influence of the inorganic composition of the membrane on the characterization and DMFC tests outputs is much higher than that of the membrane thickness. This is due essentially to the use of two sPEEK polymers with two distinct sulfonation degrees (SD = 42 and 68%) and high variation of the inorganic composition (0.0, 10.0 and 20.0 wt.% ZrPh; 0.0, 5.6 and 11.2 wt.% PBI) of the prepared composite membranes.

2.4. Characterization methods

2.4.1. Proton conductivity

Proton conductivity evaluation procedure is described in detail elsewhere [18]. The proton conductivity was measured using sulfuric acid (0.33 M) as electrolyte, at 25 °C, and determining the impedance modulus at null phase shift [18]. The spectrometer used was an HP 4284A, working in the frequency range between 100 and 10⁵ Hz. 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.

2.4.2. Swelling in aqueous methanol

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 20 wt.% aqueous methanol solution and equilibrated for 2 days at 70 °C. The weights of the swollen membranes were measured after removing carefully 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. Pervaporation measurements

The methanol permeability coefficient was evaluated through pervaporation measurements as described in [15]. 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.

2.5. DMFC operation

The membrane electrode assemblies (MEAs) were prepared by hot pressing the membrane samples between two Etek[®] ELAT electrodes (Veronica Ave Somerset, New Jersey, USA). Supported PtRu (1 mg cm⁻² 30 wt.% PtRu(1:1 a/o) on carbon with 0.7 mg cm⁻² Nafion[®] on single sided hydrophobic carbon cloth) and Pt (0.4 mg cm⁻² 20 wt.% Pt on carbon with 0.7 mg cm⁻² Nafion[®] on single sided hydrophobic carbon cloth) were used as anode and cathode electrodes, respectively. The DMFC experimental set-up is described elsewhere [19]. The MEAs (electrode area: 25 cm²) were fed with an aqueous 1.5 M methanol solution (4 ml min⁻¹, 2.5 bar) on the anode side and humidified air (10 sccm s⁻¹, 3 bar, 100% relative humidity) on the cathode side.

The following characteristics of direct methanol fuel cells using the prepared MEAs' have been experimentally determined:

- current–voltage polarization curves;
- constant voltage current at 35 mV (CV, 35 mV);
- open circuit voltage (OCV).

For the last two parameters mentioned above, the cell impedance (null phase angle impedance, NPAI) and CO₂ concentration in the cathode exhaust were also measured. The NPAI was monitored for evaluating the MEA ohmic resistance during DMFC operation [19]. The cell temperature was varied from 50 to 130 °C in order to obtain the Arrhenius plots for the studied variables (50, 70, 90, 100, 110, 130 °C). The studied membranes were not previously conditioned before DMFC tests.

2.6. Efficiency of the DMFC

The DMFC efficiency depends strongly on the two main limiting factors of the fuel cell performance: (i) poor electrocatalytic kinetics of the methanol oxidation at the anode and (ii) high permeability of the proton exchange membranes towards methanol. The first limitation leads to considerable high anodic overpotentials, lowering the cell voltage significantly below the theoretically expected values. On the other hand, the high methanol permeation from the anode to the cathode through the proton exchange membrane promotes the methanol oxidation in the cathode leading to a loss of potential due to the methanol/oxidation mixed potential. Apart from that, it leads also to a loss of reactant and therefore lower

DMFC efficiency. The reacted methanol in the cathode catalyst can be estimated using a CO₂ sensor in the cathode outlet. However, one must also quantify the CO₂ fraction that permeates through the membrane from the anode to the cathode during fuel cell operation.

Therefore, the carbon dioxide molar flow rate due to the parasitic methanol oxidation at the cathode, $N_{\text{CO}_2}^{\text{MeOH}}$, was evaluated using the following equation:

$$N_{\text{CO}_2}^{\text{MeOH}} = N_{\text{CO}_2}^{\text{Out}} - N_{\text{CO}_2}^{\text{Memb}} \quad (1)$$

where $N_{\text{CO}_2}^{\text{Memb}}$ is the CO₂ flow rate from the anode to the cathode through the proton exchange membrane and $N_{\text{CO}_2}^{\text{Out}}$ the CO₂ flow rate in the cathode outlet, measured during DMFC operation.

The CO₂ flow rate in the cathode outlet can be evaluated as

$$N_{\text{CO}_2}^{\text{Out}} = \% \text{CO}_2 (N_{\text{N}_2}^{\text{Out}} + N_{\text{O}_2}^{\text{Out}} + N_{\text{H}_2\text{O}}^{\text{Out}} + N_{\text{CO}_2}^{\text{Out}}) \quad (2)$$

where %CO₂ refers to the carbon dioxide mole fraction in the cathode outlet (measured on-line during DMFC experiments) and N_i^{Out} to the outlet molar flow rate of species i . This evaluation assumes that the crossover methanol is fully converted to carbon dioxide in the catalyst layer at the cathode and therefore $N_{\text{MeOH}}^{\text{Out}} = 0$.

The O₂, N₂ and H₂O flow rates in the cathode outlet are evaluated using the following equations:

$$N_{\text{O}_2}^{\text{Out}} = N_{\text{O}_2}^{\text{In}} - N_{\text{O}_2}^{\text{H}^+} - N_{\text{O}_2}^{\text{MeOH}} - N_{\text{O}_2}^{\text{Memb}} \quad (3)$$

$$N_{\text{N}_2}^{\text{Out}} = N_{\text{N}_2}^{\text{In}} - N_{\text{N}_2}^{\text{Memb}} \quad (4)$$

$$N_{\text{H}_2\text{O}}^{\text{Out}} = N_{\text{H}_2\text{O}}^{\text{In}} + N_{\text{H}_2\text{O}}^{\text{MeOH}} + N_{\text{H}_2\text{O}}^{\text{O}_2} + N_{\text{H}_2\text{O}}^{\text{Memb}} \quad (5)$$

where N_i^{In} is the inlet molar flux of specie i , $N_{\text{O}_2}^{\text{H}^+}$ the reacted oxygen in the cathode catalyst layer with H⁺, $N_{\text{O}_2}^{\text{MeOH}}$ the reacted oxygen with the crossover methanol, $N_{\text{H}_2\text{O}}^{\text{MeOH}}$ the formed water by the reaction between O₂ and the crossover methanol, $N_{\text{H}_2\text{O}}^{\text{O}_2}$ the formed water due to the reduction of O₂ and N_i^{Memb} the permeated component i from the anode to the cathode through the membrane.

The mass transport of the DMFC species through the membrane is described by the following equations. For water and carbon dioxide, it is assumed that the permeation is caused by diffusion and convection. In the diffusion term it is assumed that the molar flow is proportional to the concentration gradient between the cathode and anode:

$$N_{\text{H}_2\text{O}}^{\text{Memb}} = -P_{\text{H}_2\text{O}}^{\text{Memb}} \frac{C_{\text{H}_2\text{O}}^{\text{cath}} - C_{\text{H}_2\text{O}}^{\text{anod}}}{\delta_{\text{Memb}}} + n_{\text{drag}} \frac{q}{F} \quad (6)$$

$$N_{\text{CO}_2}^{\text{Memb}} = -P_{\text{CO}_2}^{\text{Memb}} \frac{C_{\text{CO}_2}^{\text{cath}} - C_{\text{CO}_2}^{\text{anod}}}{\delta_{\text{Memb}}} + n_{\text{drag}} p_{\text{CO}_2}^{\text{anod}} H(T) \frac{M_{\text{H}_2\text{O}}}{V_{\text{H}_2\text{O}}^{\text{M}}} \frac{q}{F} \quad (7)$$

where q is the fuel cell output charge, C_i^j the concentration of species i in the compartment j (anode or cathode), n_{drag} the

drag coefficient (number of entrained molecules per proton), δ_{Memb} the membrane thickness, $H(T)$ the Henry's law constant, $p_{\text{CO}_2}^{\text{anod}}$ the partial pressure of CO₂ in the anode, $M_{\text{H}_2\text{O}}$ the molecular weight of water (18 g mol⁻¹), $V_{\text{H}_2\text{O}}^{\text{M}}$ the molar volume of water, F the Faraday constant (96 485 C mol⁻¹) and, finally P_i refers to the permeability coefficients evaluated through the characterizations methods (H₂O and CH₃OH: pervaporation experiments; O₂, N₂ and CO₂: gas permeation experiments) [1].

The Henry's law constant for the solubility of carbon dioxide in water (low concentration aqueous methanol solution) is determined using the following equation [20]:

$$H(T) = 1.668656 - 5.9802 \times 10^{-3} T + 1.155184 \times 10^{-3} T^2 - 1.118743 \times 10^{-5} T^3 + 4.208352 \times 10^{-8} T^4 \quad (8)$$

in which T is the fuel cell operation temperature.

As mentioned before, it is assumed that methanol is completely converted to carbon dioxide in the cathode catalyst layer and thus the methanol molar flux through the membrane is equal to the carbon dioxide molar flow rate due to the crossover methanol oxidation at the cathode:

$$N_{\text{MeOH}}^{\text{Memb}} = N_{\text{CO}_2}^{\text{MeOH}} \quad (9)$$

On the other hand, for nitrogen and oxygen it is assumed that only the diffusion mass transfer term is required:

$$N_{\text{N}_2}^{\text{Memb}} = -P_{\text{N}_2}^{\text{Memb}} \frac{C_{\text{N}_2}^{\text{cath}} - C_{\text{N}_2}^{\text{anod}}}{\delta_{\text{Memb}}} \quad (10)$$

$$N_{\text{O}_2}^{\text{Memb}} = -P_{\text{O}_2}^{\text{Memb}} \frac{C_{\text{O}_2}^{\text{cath}} - C_{\text{O}_2}^{\text{anod}}}{\delta_{\text{Memb}}} \quad (11)$$

The use of permeability coefficients evaluated by standard characterization methods to simulate the permeation of species through the membrane is a rough estimate because real values for DMFC operation depend on the operation conditions in the entire MEA. In real DMFC operation, the concentration of species in the anode and cathode changes with the applied load and, therefore, different mass transport conditions exist compared to standard characterization methods as pervaporation and gas permeation [18]. As an example, at high load (CV experiments at 35 mV), the methanol concentration in the anode is strongly reduced, the water concentration in the anode is somewhat reduced and the CO₂ concentration in the anode is increased as compared to a pervaporation experiment. On the other hand, the methanol concentration at the cathode is lower than in a standard pervaporation experiment because methanol is mostly consumed by the anode reaction. Also, due to the electroosmotic drag, the water and methanol permeation from the anode to the cathode would increase with increased current density.

However, the use of parameters obtained through easily implementable characterization methods enables the successful connection between results obtained by membrane and fuel cell developers. In fact, recently published results showed

qualitatively good agreement between DMFC results and the output of standard characterization methods [21].

According to the stoichiometry of the oxidation and reduction reactions (Fig. 1) one obtains:

$$N_{\text{H}_2\text{O}}^{\text{MeOH}} = 2N_{\text{CO}_2}^{\text{MeOH}} \quad (12)$$

$$N_{\text{O}_2}^{\text{MeOH}} = 1.5N_{\text{CO}_2}^{\text{MeOH}} \quad (13)$$

$$N_{\text{O}_2}^{\text{H}^+} = \frac{1.5q}{6F} \quad (14)$$

$$N_{\text{H}_2\text{O}}^{\text{O}_2} = \frac{3q}{6F} \quad (15)$$

Inserting the above equations into Eq. (2) yields the following expression for the carbon dioxide molar flow rate due to the methanol oxidation in the cathode:

$$N_{\text{CO}_2}^{\text{MeOH}} = \frac{\% \text{CO}_2 \left(N_{\text{T}}^{\text{In}} + \frac{1.5q}{6F} - N_{\text{T}}^{\text{Memb}} \right) - N_{\text{CO}_2}^{\text{Memb}}}{1 + 1.5 \times \% \text{CO}_2} \quad (16)$$

where N_{T}^{In} is the total molar flow rate in the cathode inlet and $N_{\text{T}}^{\text{Memb}}$ the total molar flow rate through the membrane. This last variable is defined as

$$N_{\text{T}}^{\text{Memb}} = N_{\text{H}_2\text{O}}^{\text{Memb}} + N_{\text{CO}_2}^{\text{Memb}} + N_{\text{N}_2}^{\text{Memb}} + N_{\text{O}_2}^{\text{Memb}} \quad (17)$$

Assuming the Faraday law for the methanol oxidation in the cathode, the current density loss due to methanol crossover, I_{MeOH} , can be evaluated through the following equation:

$$I_{\text{MeOH}} = \frac{N_{\text{CO}_2}^{\text{MeOH}} 6F}{A_{\text{cell}}} \quad (18)$$

where A_{cell} is the DMFC effective area.

Once one only knows the %CO₂ for the open circuit voltage and constant voltage (35 mV), the current density loss due to methanol crossover is only evaluated for these two situations, i.e. $I_{\text{OCV,MeOH}}$ and $I_{35\text{mV,MeOH}}$, respectively. Therefore, it is assumed that the current density loss due to methanol crossover varies linearly between the estimated methanol loss current density at open circuit, $(I_{\text{OCV}})_{\text{MeOH}}$, and constant voltage (35 mV), $(I_{35\text{mV}})_{\text{MeOH}}$ (Fig. 2) [22]. Thus, in order to evaluate $I_{i,\text{MeOH}}$ for the intermediate current densities the following equation was applied:

$$I_{i,\text{MeOH}} = I_{\text{OCV,MeOH}} - \frac{I_{\text{OCV,MeOH}} - I_{35\text{mV,MeOH}}}{I_{35\text{mV}}} I_{i,\text{cell}} \quad (19)$$

The potential efficiency, η_{E} , is evaluated from:

$$\eta_{\text{E}} = \frac{E_{i,\text{cell}}}{E_{\text{rev}}} \quad (20)$$

where $E_{i,\text{cell}}$ is the measured cell voltage during the polarization curve evaluation and E_{rev} the reversible voltage of the DMFC (1.21 V).

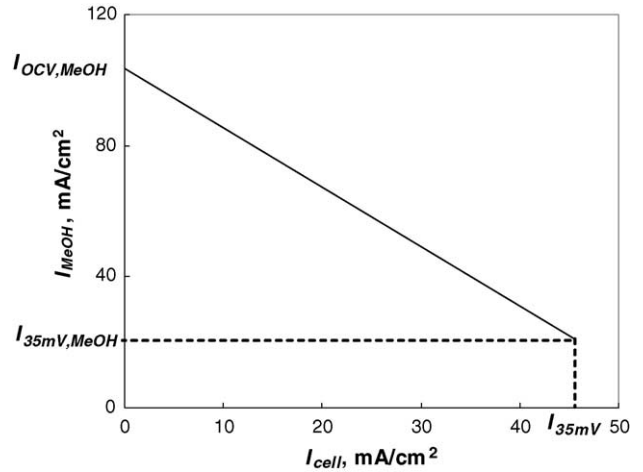


Fig. 2. Current density loss due to methanol crossover as a function of the DMFC current density (linear approximation).

On the other hand, the Faraday efficiency, η_{F} , is evaluated from:

$$\eta_{\text{F}} = \frac{I_{i,\text{cell}}}{I_{i,\text{cell}} + I_{i,\text{MeOH}}} \quad (21)$$

Finally, the overall DMFC efficiency, η_{DMFC} , is evaluated using the following equation:

$$\eta_{\text{DMFC}} = \eta_{\text{E}} \eta_{\text{F}} \quad (22)$$

3. Results and discussion

3.1. Characterization results

The prepared composite membranes were previously characterized in terms of the following properties: proton conductivity, swelling in water and aqueous methanol, permeability coefficients towards DMFC species (water, methanol, oxygen, carbon dioxide and nitrogen) and morphology [1]. In the present paper, some of previous data was selected in order to better understand the results obtained in the DMFC tests using the prepared composite membranes. The selected properties of the membrane characterization study were: proton conductivity, aqueous methanol swelling and permeability towards methanol.

In general, the main goal in the development of membranes for DMFC application is to achieve the best balance between proton conductivity and methanol sorption/permeation. The proton exchange membrane should have sufficient proton conductivity and low methanol sorption/permeation. Fig. 3 shows the effect on these properties after incorporation of zirconium phosphate, pretreated with *n*-propylamine/PBI, in the sPEEK polymer. As can be seen, the sample's proton conductivity (25 °C, impedance spectroscopy) decreases with the amount of inorganic incorporation. This fact can be assumed as a disadvantage for the DMFC performance due to the increase of the proton transport resistance in

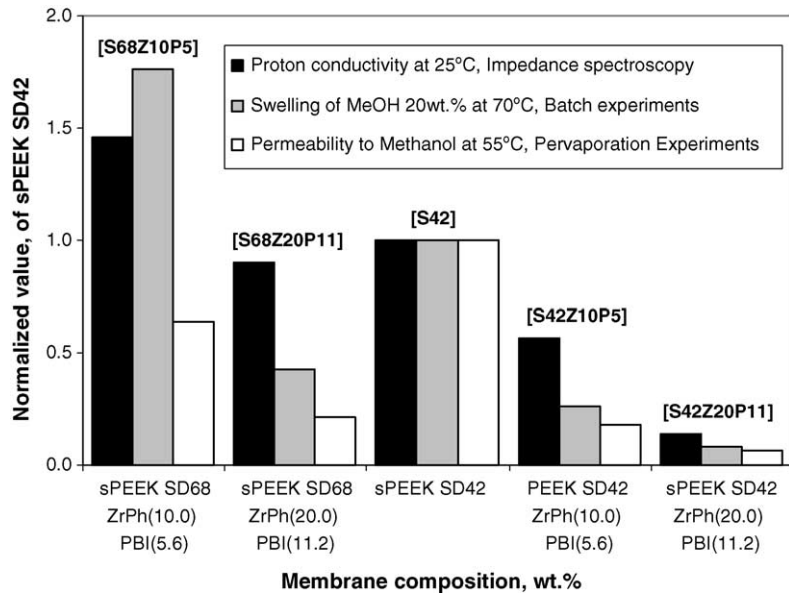


Fig. 3. Proton conductivity, aqueous methanol swelling and methanol permeability coefficients of the sPEEK composite membranes, using the data of sPEEK SD42 membrane as reference.

the membrane (higher ohmic losses). On the other hand, it can be also observed that the inorganic incorporation also decreases the samples swelling in methanol (70 °C, batch experiments) and permeability towards methanol (55 °C, pervaporation experiments). These two results can be assumed as advantages because detrimental methanol crossover is reduced due to the improved properties in terms of lower methanol solubility and diffusivity.

Taking the unmodified membrane sPEEK SD = 42%, S42, as reference material (Fig. 3), it can be verified that the composite membrane prepared with sPEEK SD = 68% and inorganic composition of 20.0 wt.% ZrPh and 11.2 wt.% PBI, S68Z20P11, provides a similar proton conductivity, but reduced swelling in aqueous methanol and permeability. It can be also seen that the composite membrane S68Z10P5 has higher proton conductivity than that of S42, although its swelling in methanol can be considered as excessive compared to others. The composite membranes prepared with sPEEK SD = 42% as base polymer, show low proton conductivity, and also low swelling of aqueous methanol and permeability towards methanol.

3.2. DMFC temperature study

The open circuit voltage obtained for the investigated MEAs is shown in Fig. 4a as a function of temperature (Arrhenius plots). It can be observed that the composite membrane S68Z20P11 presents the highest values for OCV in the studied range of temperatures. As mentioned before, it is believed that this membrane presents improved properties in terms of good proton conductivity and low methanol permeation (reduced potential loss). However, it can be seen that for this membrane the OCV Arrhenius plot flats as temperature increases. For the other composite membranes, it can

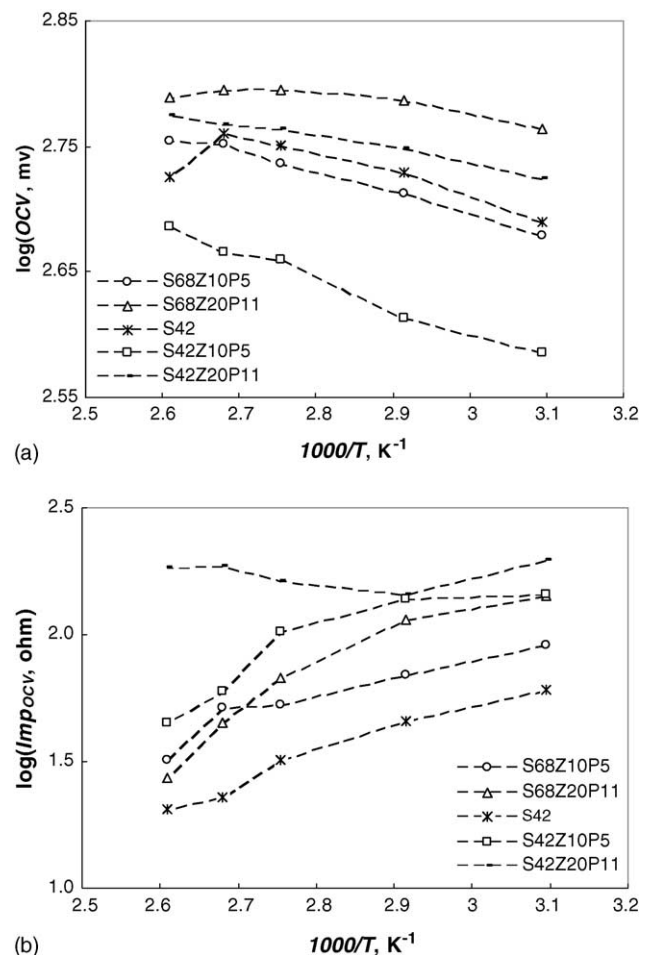


Fig. 4. Open circuit voltage experiments: (a) open circuit voltage and (b) null phase angle impedance as a function of temperature for the DMFC using sPEEK composite membranes.

Table 1
Carbon dioxide concentration (vol.%) in the cathode outlet for open circuit experiments as a function of the DMFC operation temperature

Membrane	Cell temperature (°C)				
	50	70	90	100	110
	CO ₂ cathode outlet (vol.%)				
S68Z10P5	0.1	0.1	0.2	0.2	0.4
S68Z20P11	0.1	0.1	0.1	0.2	0.8
S42	0.2	0.2	0.4	1.1	1.4
S42Z10P5	0.0	0.1	0.1	0.3	1.3
S42Z20P11	0.1	0.2	0.5	0.7	1.2

be observed that the OCV increase with temperature is more pronounced. The membrane S42Z10P5 is believed to have the lowest OCV for all temperatures due to its high ohmic resistance (low proton conductivity, Fig. 3) with simultaneous considerable methanol permeability. On the other hand, in the particular case of the unmodified membrane (SD42), it can be seen that OCV has a maximum value at intermediate temperature (Fig. 4a). This result may indicate that this membrane could present low chemical stability for DMFC use at medium temperatures (excessive methanol swelling). From Fig. 4a it can also be verified that, for both sPEEK polymers, the composite membranes with higher amount of inorganic incorporation (20.0 wt.% ZrPh and 11.2 wt.% PBI) provide higher open circuit voltage values, in agreement with the trends shown in Fig. 3 regarding proton conductivity and methanol sorption/permeation.

With respect to the null phase angle impedance variation with temperature, from Fig. 4b it can be observed that it decreases with temperature for all membranes, as expected, except for S42Z20P11. It is believed that this membrane presents the highest NPAI value (higher ohmic resistance) due to its lower sulfonation degree (SD42%) and highest amount of inorganic incorporation (lower proton conductivity and swelling). For higher temperatures, it is possible that for this membrane the NPAI increase is due to less favorable membrane humidification conditions (vapor feed and temperatures above the water boiling point) [1]. On the other hand, for the DMFC with the unmodified S42 membrane, it can be observed that although having an intermediate open circuit potential value (Fig. 4a), it presents the lowest ohmic resistance for OCV experiments (Fig. 4b). It can be also observed that for both sPEEK matrix polymers (SD = 42 and 68%), the ohmic resistance associated with the composite membranes increases with the amount of inorganic modification (lower proton conductivity, Fig. 3).

In Table 1, the carbon dioxide concentration (vol.%) at the cathode outlet for OCV experiments is presented as a function of temperature. It can be observed that the unmodified sPEEK membrane (S42) has the highest CO₂ concentrations and this fact may explain its moderate OCV value (Fig. 4a). This result seems to be also in agreement with the high methanol permeability obtained through pervaporation experiments for this membrane (Fig. 3). In contrast, the inor-

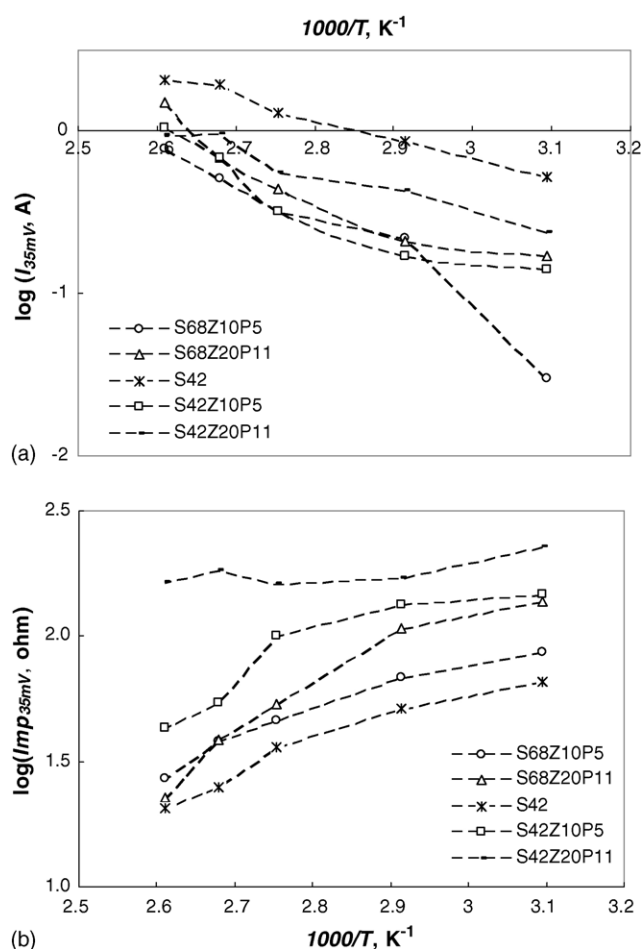


Fig. 5. Constant voltage experiments, 35 mV: (a) current density and (b) null phase angle impedance as a function of temperature for the DMFC using SPEEK composite membranes.

ganic incorporation of ZrPh and PBI in both sPEEK polymers (mainly SD = 68%) produced membranes that when tested in the DMFC produced low CO₂ emissions for temperatures up to 100 °C (higher OCV values, Fig. 4a). For 110 °C, the CO₂ concentration at the cathode outlet increases more strongly for the composite membranes, although to lower levels than those obtained for the unmodified membrane (S42).

In Fig. 5a is plotted the membranes current density at 35 mV as a function of the DMFC operation temperature. It can be observed that the unmodified membrane presents the best performance in terms of production of electric energy. Moreover, it can be seen that for this membrane the logarithm of the current density increases almost linearly with the reciprocal value of the temperature. In contrast, for the composite membranes S68Z10P5, S68Z20P11 and S42Z10P5, higher temperatures seem to have a more pronounced effect on the fuel cell current.

Fig. 5b shows the NPAI of the studied membranes tested for constant voltage experiments (35 mV). In contrast with the open circuit results obtained for the unmodified membrane, S42, i.e. higher OCV values does not mean lower NPAI values (Fig. 4a and b, mainly related with methanol crossover),

Table 2

Carbon dioxide concentration (vol.%) in the cathode outlet for constant voltage experiments (35 mV) as a function of the DMFC operation temperature

Membrane	Cell temperature (°C)				
	50	70	90	100	110
	CO ₂ cathode outlet (vol.%)				
S68Z10P5	0.0	0.0	0.1	0.1	0.1
S68Z20P11	0.0	0.0	0.0	0.1	0.1
S42	0.1	0.2	0.3	0.8	1.8
S42Z10P5	0.0	0.0	0.0	0.2	0.4
S42Z20P11	0.0	0.1	0.1	0.2	1.1

from Fig. 5b it can be observed that NPAI is in agreement with the current density plots presented in Fig. 5a. This membrane presents the lowest ohmic resistance and the highest current density during DMFC tests at constant voltage. As it was obtained for the OCV experiments, the highest value for NPAI is obtained for the composite membrane prepared with the sPEEK of lower sulfonation degree (SD = 42%) and higher amount of inorganic modification (20.0 wt.% ZrPh and 11.2 wt.% PBI), which exhibits lower proton conductivity. Also, the results for this membrane shows a more flat NPAI variation with temperature than that observed for other tested membranes.

In terms of the CO₂ concentration in the cathode outlet for CV experiments (Table 2), it can be noticed that lower values are usually recorded compared to OCV experiments (Table 1). It is believed that this fact is due to the lower methanol crossover at higher current densities (lower concentration of methanol in the anode, thus lowering the mass transfer driving force). On the other hand, it can be observed from Table 2 that, although with the best performance in terms of energy production (Fig. 5a), the unmodified membrane, S42, presents the highest CO₂ concentration in the cathode outlet (higher methanol crossover). For the highest tested temperature (110 °C), the composite membrane S68Z20P11 presents a much lower CO₂ concentration, 0.1 vol.%, and a current density near the one obtained for the unmodified membrane (Fig. 5a). Therefore, it should be interesting to plot the Faraday efficiency for each membrane evaluated through Eq. (21) (Fig. 6). In the present work, for the Faraday and global DMFC efficiency evaluation it was assumed that $N_{\text{H}_2\text{O}}^{\text{Out}} = 0$ due to the fact that water is removed from the cathode outlet before the stream reaches the CO₂ sensor [19]. From this figure it can be observed that, although with higher current density, the S42 membrane presents always a lower Faraday efficiency than S68Z20P11, which has efficiencies of 100% at the lower temperatures tested—null CO₂ concentration in the cathode outlet (Table 2). Apart from that, it can also be observed that for S42, S42Z10P5 and S42Z20P11, the Faraday efficiency tends to decrease with increasing temperatures, due to the increase in CO₂ concentration in the cathode outlet (higher methanol crossover). Finally, from Fig. 6, it can also be observed that the composite membrane prepared with sPEEK polymer SD = 68% and inorganic compo-

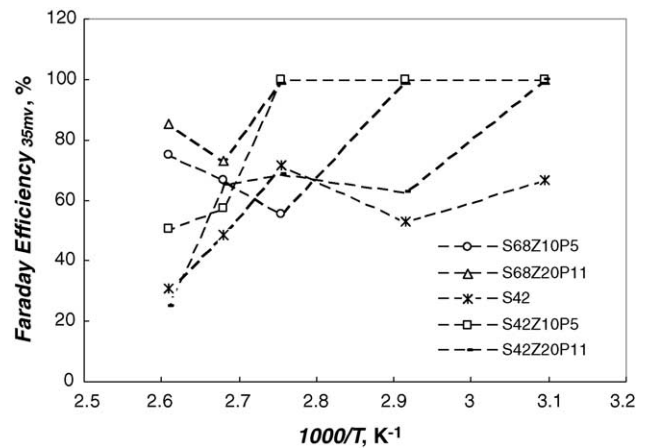


Fig. 6. Faraday efficiency (constant voltage experiments, 35 mV) as a function of temperature for the DMFC using sPEEK composite membranes.

sition 20.0 wt.% ZrPh and 11.2 wt.% PBI presented always the highest Faraday efficiency for the studied temperature range. This fact shows that for this membrane, the parasitic current density due to the methanol oxidation at the cathode is the lowest in comparison with the other membranes.

3.3. Polarization curves and global efficiency

The current density–potential and current density–fuel cell efficiency plots obtained for the DMFC using the MEAs made from sPEEK composite membranes at 110 °C are shown in Fig. 7. For the tested operation conditions, it was only possible to obtain the polarization curves for the following membranes: S42, S42Z10P5 and S68Z20P11, which are those that exhibited the highest current densities at this temperature (see Fig. 5a). For the other prepared membranes one can assume lower polarization curves than the plotted for S42Z10P5 membrane. From data shown in Fig. 7 one can conclude that the unmodified membrane presents

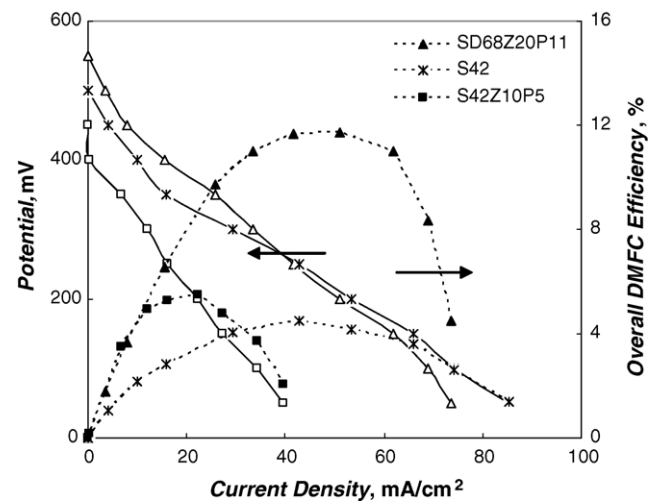


Fig. 7. Polarization curves and estimated efficiency of the DMFC using sPEEK composite membranes at 110 °C.

Table 3

Peak power density and corresponding potential evaluated for DMFC using sPEEK composite membranes at 110 °C

Membrane	Peak power density (mW cm ⁻²)	Potential (mV)
S68Z20P11	8.6	250
S42	10.4	200
S42Z10P5	4.8	200

the best DMFC performance in terms of energy production among all the studied MEAs, achieving a maximum power density output of 10.4 mW cm⁻² for a current density of 51.8 mA cm⁻² (Table 3). In comparison, the composite membrane S68Z20P11 achieves an output value of 8.6 mW cm⁻² at 34.3 mA cm⁻². Although with lower energy output, the application of the composite membrane S68Z20P11 in the DMFC resulted in much lower concentrations of CO₂ in the cathode outlet compared to the S42 membrane (0.1 and 1.8 vol.% at 35 mV, respectively, Table 2). Therefore, plotting the global DMFC efficiency as a function of the current density (Fig. 7), evidences that the composite membrane S68Z20P11 achieves a fuel cell efficiency peak of almost 12%. It can also be observed that the unmodified membrane, S42, has a maximum global efficiency that is even lower than the composite membrane S42Z10P5.

Once the S68Z20P11 membrane achieved the best performance in terms of efficiency and similar energy production as that of the unmodified membrane, S42, the previously studied MEA using that membrane was further tested in the DMFC, at higher temperatures up to 130 °C (Fig. 8). The membrane was also tested using pure oxygen as feed in the cathode inlet. From Fig. 8 it can be observed that the membrane performance, in terms of energy production, increased in comparison to the previous study, for the same temperature of 110 °C (Fig. 7). It is believed that this increase of the DMFC performance in terms of energy production is essentially due to the distinct conditioning conditions before the DMFC test. From this plot it can be observed that the

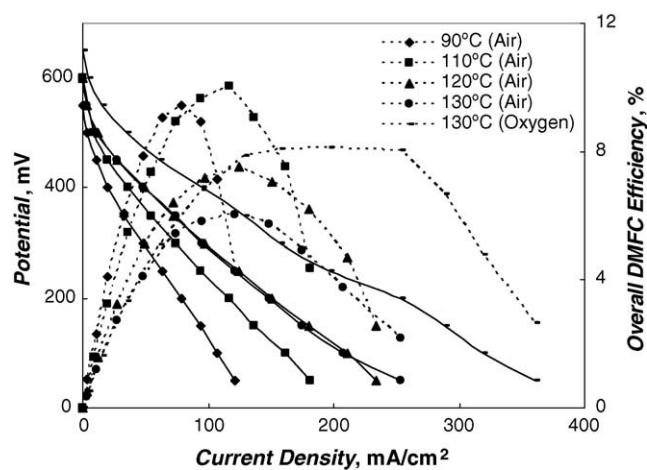


Fig. 8. Polarization curves and estimated efficiency of the DMFC, for several temperatures, using the composite membrane sPEEK SD = 68% 20.0 wt.% ZrPh 11.2 wt.% PBI.

Table 4

Peak power density at 250 mV evaluated for the DMFC, at several temperatures, using the sPEEK composite membrane SD = 68% 20.0 wt.% ZrPh 11.2 wt.% PBI

Temperature (°C)	Peak power density at 250 mV (mW cm ⁻²)
90 (air)	15.8
110 (air)	23.5
120 (air)	30.0
130 (air)	31.2
130 (O ₂)	50.1

DMFC performance in terms of energy production increases with temperature (Table 4), although having the maximum of the overall DMFC efficiency at 110 °C. It is believed that this is due to fact that apart from improving the membrane proton conductivity and methanol oxidation kinetics at the anode, the increase of the DMFC temperature also increases the methanol crossover. When using pure oxygen in the cathode feed instead of air, at 130 °C, Fig. 8 shows that the DMFC performance increases in terms of both energy production and efficiency. The DMFC using this membrane achieves a power output of 50.1 mW cm⁻² at 198.0 mA cm⁻² in comparison with 31.2 mW cm⁻² at 124.9 mA cm⁻² for air feed (Table 4). The explanation of these results is the increased stoichiometry of oxygen in the cathode electro-reduction reaction. However, in terms of fuel cell efficiency, it can be observed that the maximum global efficiency is obtained for the temperature of 110 °C (Fig. 8). It is believed that this result is due to the higher effect of the methanol crossover for higher temperatures (120 and 130 °C). Finally, it is worth noting that during the DMFC tests at 130 °C, the membrane remained stable and no bubbles were detected in the anode exhaust. This fact shows the improved properties of the prepared composite membrane in terms of stability for DMFC applications at low/medium operation temperatures.

4. Conclusions

The characterization results showed that the inorganic incorporation of pretreated zirconium phosphate decreases the membrane proton conductivity, aqueous methanol swelling and permeability towards methanol. However, the incorporation of pretreated ZrPh enabled the preparation of membranes with improved relationship between proton conductivity and permeability towards methanol (sorption and diffusion). Although with lower production of current density, the composite membranes S68Z20P11 and S42Z10P5 achieved higher global efficiency than the unmodified sPEEK membrane, S42. Moreover, for temperatures up to 110 °C, the membrane S68Z20P11 achieved a similar current density as S42, but with significantly reduced CO₂ production in the cathode (lower methanol crossover). This membrane proved to be stable for temperatures up to 130 °C.

In general, the present publication shows that the incorporation of zirconium phosphate pretreated with *n*-propylamine

and polybenzimidazole allows the preparation of sPEEK composite membranes with improved properties in terms of chemical stability and DMFC efficiency. These composite membranes proved to be promising for DMFC application at low/medium temperatures (up to 130 °C).

Acknowledgements

Financial support by the HGF-Venetzungsfonds is gratefully acknowledged. The work of Vasco Silva was supported by FCT (Grant SFRH/BD/6818/2001). Vasco Silva would like to acknowledge both FCT and GKSS for the assigned grant 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] V.S. Silva, B. Ruffmann, S. Vetter, A. Mendes, L.M. Madeira, S.P. Nunes, *Catal. Today*, in press.
- [2] A.S. Aricò, P. Cretí, P.C. Antonucci, V. Antonucci, *Electrochem. Solid State Lett.* 1 (1998) 66.
- [3] M. Baldauf, W. Preidel, *J. Power Sources* 84 (1999) 161.
- [4] R. Parsons, T. VanderNoot, *J. Electroanal. Chem.* 257 (1988) 9.
- [5] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, *J. Membrane Sci.* 185 (2001) 73.
- [6] B. Gurau, E.S. Smotkin, *J. Power Sources* 112 (2002) 339.
- [7] Z. Qi, A. Kaufman, *J. Power Sources* 110 (2002) 117.
- [8] A. Heinzl, V.M. Barragán, *J. Power Sources* 84 (1999) 70.
- [9] J. Cruickshank, K. Scott, *J. Power Sources* 70 (1998) 40.
- [10] S.M.J. Zaidi, S.D. Mikailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, *J. Membrane Sci.* 173 (2000) 17.
- [11] S.D. Mikhailenko, S.M.J. Zaidi, S. Kaliaguine, *Catal. Today* 67 (2001) 225.
- [12] K.A. Kreuer, *J. Membrane Sci.* 185 (2001) 3.
- [13] L. Jörissen, V. Gogel, J. Kerres, J. Garche, *J. Power Sources* 105 (2002) 267.
- [14] L. Li, J. Zhang, Y. Wang, *J. Membrane Sci.* 226 (2003) 159.
- [15] S.P. Nunes, B. Ruffmann, E. Rikowsky, S. Vetter, K. Richau, *J. Membrane Sci.* 203 (2002) 215.
- [16] R. Nolte, K. Ledjeff, M. Bauer, R. Mulhapt, *J. Membrane Sci.* 83 (1993) 211.
- [17] B. Ruffmann, H. Silva, B. Schulte, S. Nunes, *Solid State Ionics* 162/163 (2003) 269.
- [18] V.S. Silva, B. Ruffmann, H. Silva, Y.A. Gallego, A. Mendes, L.M. Madeira, S.P. Nunes, *J. Power Sources* 140 (2005) 34.
- [19] E. Gulzow, T. Kaz, R. Reissner, H. Sander, L. Schilling, M.V. Bradke, *J. Power Sources* 105 (2002) 261.
- [20] K.-H. Hellwege, A.M. Hellwege (Eds.), *Landolt-Börnstein: Zahlenwerte und Funktionen aus Physik*, Springer-Verlag, Berlin, 1962.
- [21] V.S. Silva, J. Schirmer, R. Reissner, B. Ruffmann, H. Silva, A. Mendes, L.M. Madeira, S.P. Nunes, *J. Power Sources* 140 (2005) 41.
- [22] H. Dohle, K. Wippermann, *J. Power Sources* 135 (2004) 152.