

# Proton electrolyte membrane properties and direct methanol fuel cell performance

## II. Fuel cell performance and membrane properties effects

V.S. Silva<sup>b</sup>, J. Schirmer<sup>c</sup>, R. Reissner<sup>c</sup>, B. Ruffmann<sup>a</sup>, H. Silva<sup>a,b</sup>,  
A. Mendes<sup>b,\*</sup>, L.M. Madeira<sup>b</sup>, S.P. Nunes<sup>a</sup>

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

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

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

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### Abstract

In order to study the relationship between the properties of proton electrolyte membranes (PEMs), obtained through standard characterization methods, and the direct methanol fuel cell (DMFC) performance, inorganic–organic hybrid membranes, modified via in situ hydrolysis, were used in a membrane electrolyte assembly (MEA) for DMFC application. The membranes, the characterization of which was performed in the previous paper of this series, were based on sulfonated poly(ether ether ketone) (sPEEK) with a sulfonation degree (SD) of 87% and were loaded with different amounts of zirconium oxide (5.0, 7.5, 10.0, 12.5 wt.%). The standard characterization methods applied were impedance spectroscopy (proton conductivity), water uptake, and pervaporation (permeability to methanol). The MEAs were characterized investigating the DMFC current–voltage polarization curves, constant voltage current (CV, 35 mV), and open-circuit voltage (OCV). The fuel cell ohmic resistance (null phase angle impedance, NPAI) and CO<sub>2</sub> concentration in the cathode outlet were also measured. The characterization results show that the incorporation of the inorganic oxide in the polymer network decreases the DMFC current density for CV experiments, CO<sub>2</sub> concentration in the cathode outlet for both OCV and CV experiments and, finally, the maximum power density output. The opposite effect was verified in terms of the NPAI (ohmic resistance) for both OCV and CV experiments. A good agreement was found between the studied DMFC performance parameters and the characterization results evaluated by impedance spectroscopy, water uptake and pervaporation experiments. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Direct methanol fuel cell; Characterization methods; Water uptake; Pervaporation; Impedance spectroscopy; Composite membranes

### 1. Introduction

Liquid feed direct methanol fuel cells (DMFCs) operating at low temperatures and employing solid protonic electrolytes are promising candidates for portable power applications. DMFCs do not require fuel processing, allowing

simple and compact designs. Apart from that, the use of methanol as fuel for portable applications has several advantages in comparison with hydrogen. In order to be competitive within the portable power applications market, the DMFC must be economical and capable of delivering high power densities [1]. Recent reports demonstrated a relatively high DMFC performance using solid polymer electrolytes such as Nafion® [2–7]. However, the use of perfluorinated membranes as polymer electrolyte increases appreciably the

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

cost of the entire system [8–10]. Apart from the cost disadvantage, the use of Nafion<sup>®</sup>-like polymer electrolyte leads to a significant decrease in the fuel cell coulombic efficiency due to the methanol crossover from the anode to the cathode. Methanol uses cathode Pt sites (reducing the effective area of the cathode) for the direct reaction between methanol and oxygen, generating a mixed potential that reduces the cell voltage [11,12]. However, these problems can be mitigated by developing new polymers, or modifying the existing ones, in order to achieve high ionic conductivity, low permeability to DMFC reactants, long-term stability under operating conditions and, not less important, low cost. Nowadays, non-perfluorinated polymers are being investigated by different groups [13–18]. Apart from the possibility of being directly applied to the DMFC, these polymers can be used as a polymeric matrix for organic/inorganic modifications, so that the properties of the final proton exchange membranes can be improved [15,16,19–21].

In order to select the proper material for direct methanol fuel cell applications, characterization methods play an important role in DMFC research. Ideally, the obtained characteristics of the specific material can be used as a selection criterion: they should allow us to forecast the corresponding DMFC performance. For example, instead of conducting DMFC experiments, the results of some characterization methods can be used to estimate the fuel cell performance for a given membrane. At present, several characterization methods are used to obtain critical parameters for DMFC application [21].

The three main characteristics considered by the standard characterization methods are (Fig. 1):

- **Proton conductivity:** It gives an estimate of the  $H^+$  conductivity, which is the main function of a proton exchange membrane. This property is usually evaluated with acid or water electrolytes (hydrated membranes) by impedance spectroscopy [14,15,18–30].
- **Membrane permeability to methanol:** The study of the methanol mass transport through DMFC membranes is very common due to its detrimental effect on the DMFC performance (reduced coulombic efficiency). Even if not accounting for the anode catalytic reaction and the electroosmotic drag mass transfer, the permeability is usually evaluated by pervaporation [20,21,26–28] and diffusion cell experiments [29–31].
- **Water swelling:** It gives a measure of the water solubility in the membrane. It is usually associated to improved proton conductivity but also to an increase in methanol crossover and morphological instability. It is usually evaluated using batch experiments in liquid solutions at room temperature [14,15,19–21,27–29,32].

The lack of a systematic study that relates the membrane properties and the fuel cell energy output disables the validation of the characterization results, in terms of the fuel cell performance. Several DMFC research groups published promising data for new materials [14,15,18,20,21,26–28].

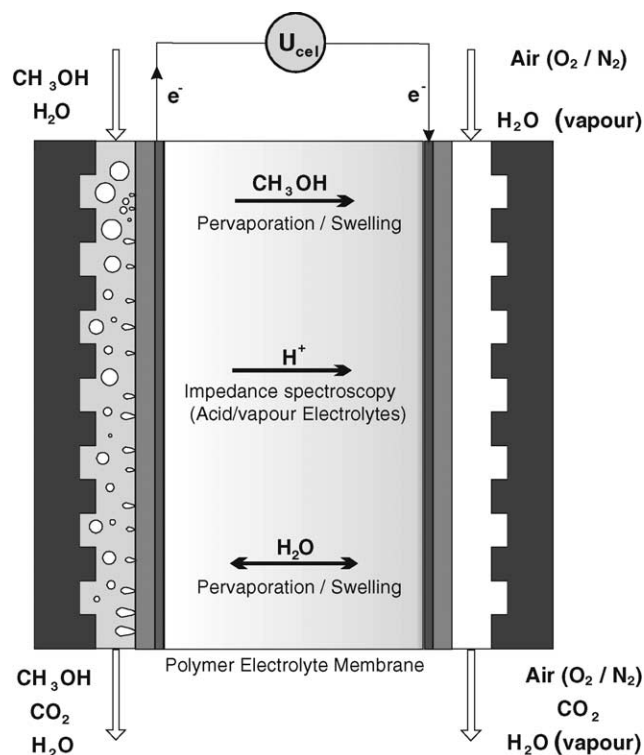


Fig. 1. Sketch of a DMFC illustrating proton, water and methanol permeation across the PEM and related characterization methods.

However, a critical evaluation of the membrane properties implications in the direct methanol fuel cell performance is an important task to be done.

In this paper, we perform an analysis of the effect of the membrane properties on the DMFC performance for temperatures up to 90 °C. We were able to prepare composite membranes with a wide variety of physical/chemical properties using a systematic variation of the inorganic content in the sulfonated poly(ether ether ketone) polymer (from 2.5 to 12.5 wt.% of  $ZrO_2$ ) [33]. The incorporation of zirconium oxide in this polymer enabled the preparation of composite membranes with gradual decrease in water swelling, proton conductivity and permeability towards methanol and water [33]. Apart from taking advantage of the improved barrier properties of the composite membranes, the  $ZrO_2$  incorporation enables also the preparation of membranes with improved morphological stability for DMFC application at temperatures up to 90 °C, although using sPEEK polymer with high sulfonation degree (higher proton conductivity). From Part I paper results, the selected characterization methods for the analysis of the membrane properties effects were: impedance spectroscopy (proton conductivity and proton transport resistance), pervaporation (permeability to methanol) and water swelling. The proton transport resistance measures the specific resistance of the membrane with respect to proton transport (Part I paper). The aim of this study is to identify and study the main characterization parameters for DMFC research. These parameters should en-

able the right selection of materials for DMFC application purposes, by providing a first estimate of the corresponding fuel cell performance.

## 2. Experimental

The membrane electrode assemblies (MEAs) were prepared by hot pressing the membrane samples between two Etek<sup>®</sup> ELAT electrodes. Supported PtRu (1 mg cm<sup>-2</sup> of 30 wt.% PtRu (1:1) on carbon with 0.7 mg cm<sup>-2</sup> Nafion<sup>®</sup>/PTFE) and Pt (0.4 mg cm<sup>-2</sup> of 20 wt.% Pt on carbon with 0.7 mg cm<sup>-2</sup> Nafion<sup>®</sup>/PTFE) were used as anode and cathode electrodes, respectively. The membranes were humidified in water for 1 min and then pressed with the electrodes at 100 °C and 79 bar for 2 min. The DMFC experimental set-up is described elsewhere [34]. The MEAs (active cell area of 25 cm<sup>2</sup>) were conditioned at room temperature by feeding with an aqueous 0.25 M methanol solution (4 ml min<sup>-1</sup>, 2.5 bar) on the anode side and humidified air (600 sccm min<sup>-1</sup>, 3 bar, 100% relative humidity) on the cathode side for 2 h, and then operated with an aqueous 1.5 M methanol solution (4 ml min<sup>-1</sup>, 2.5 bar) on the anode side and humidified air (600 sccm min<sup>-1</sup>, 3 bar, 100% relative humidity) on the cathode side. The cell temperature was varied from 40 to 110 °C. The MEAs' characterization was performed measuring the DMFC current–voltage polarization curves, constant voltage current (CV, 35 mV), and open-circuit voltage (OCV). The applied procedures used in the MEAs' characterization are described elsewhere [34]. The last two parameters investigated also included the measurement of the cell impedance (null phase angle impedance, NPAI) and CO<sub>2</sub> concentration. The NPAI and CO<sub>2</sub> concentration at the cathode outlet were monitored as a measure of the MEA ohmic resistance and methanol crossover during DMFC operation, respectively [35]. In the present study, only results from the first day were investigated.

The sPEEK (S.D. = 87%) membranes with zirconium oxide contents lower than 10.0 wt.% were found to be stable at temperatures up to 90 °C, despite having high sulfonation polymer. For higher ZrO<sub>2</sub> contents, the thermal stability was even better. Therefore, in agreement with recent data [19,33], these results show effectively that the zirconium oxide incorporation via in situ hydrolysis increases the chemical/thermal stability of the composite membranes. The thickness of the membranes used was between 100 and 150 μm (membranes with 5.0, 7.5, 10.0 and 12.5 wt.% of ZrO<sub>2</sub> with 113, 150, 108 and 100 μm, respectively). It is expected that the membranes 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. The hybrid sPEEK membrane with 2.5 wt.% of ZrO<sub>2</sub> was not studied because it proved to be instable in methanol aqueous solutions due to its excessive swelling [33].

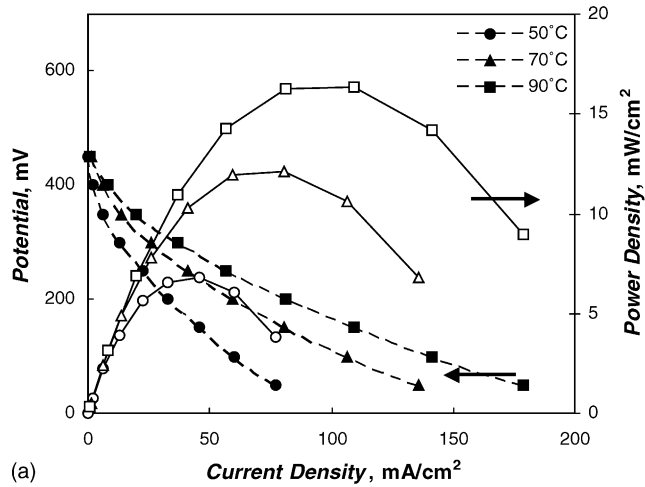
## 3. Results and discussion

### 3.1. DMFC performance

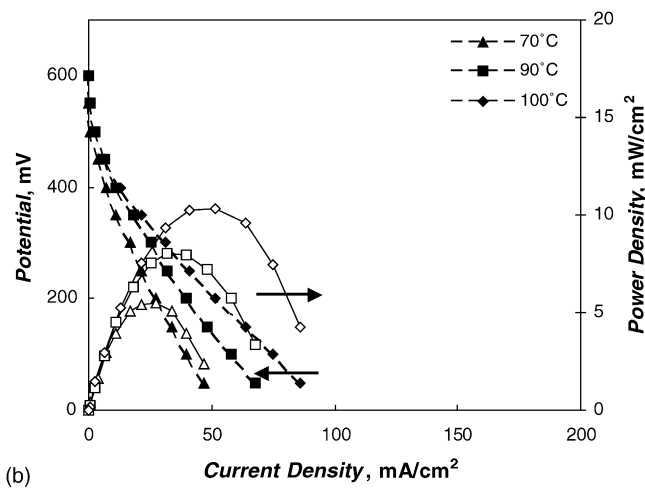
The current density–voltage and current density–power density plots of MEAs made from sPEEK composite membranes with 5.0, 7.5 and 10.0 wt.% of ZrO<sub>2</sub> at different temperatures are shown in Fig. 2. The curves corresponding to the hybrid membrane with 12.5 wt.% ZrO<sub>2</sub> are not presented because they could not be measured due to the high ohmic resistance of the corresponding MEA. From Fig. 2, it can be seen that the membrane with 5.0 wt.% of ZrO<sub>2</sub> presents the best DMFC performance among all the studied MEAs. For 90 °C, the 5.0 wt.% ZrO<sub>2</sub> composite membrane achieves a maximum power density output of 16.4 mW cm<sup>-2</sup> for a current density of 109.2 mA cm<sup>-2</sup>. In comparison, for the same temperature, the 7.5 wt.% zirconium oxide-modified membrane achieves an output value of 8.0 mW cm<sup>-2</sup> for 32.1 mA cm<sup>-2</sup>. On the other hand, due to its high ohmic resistance, the DMFC using a 10.0 wt.% ZrO<sub>2</sub> composite membrane only provided a polarization curve at 110 °C and a maximum power density of 2.7 mW cm<sup>-2</sup> was achieved for a current density of 17.8 mA cm<sup>-2</sup>.

Apart from measuring the current density–voltage polarization curves, in the present study the null phase angle impedance (NPAI) and CO<sub>2</sub> cathode outlet concentration were also evaluated for constant voltage (CV) experiments at 35 mV (Fig. 3). It can be seen that the cell current (Fig. 3b) and CO<sub>2</sub> cathode outlet concentration (Fig. 3c) decrease when increasing the sPEEK zirconium oxide content. The opposite effect can be seen for the NPAI (Fig. 3a), i.e., the ohmic resistance of the MEAs increases with the amount of ZrO<sub>2</sub> in the polymer matrix. This means that hybrid membranes with higher ZrO<sub>2</sub> contents present lower permeability towards protons and methanol, increasing the MEAs ohmic resistance (NPAI) and reducing both DMFC output current and CO<sub>2</sub> concentration in the cathode outlet, in good agreement with the characterization data obtained previously [33].

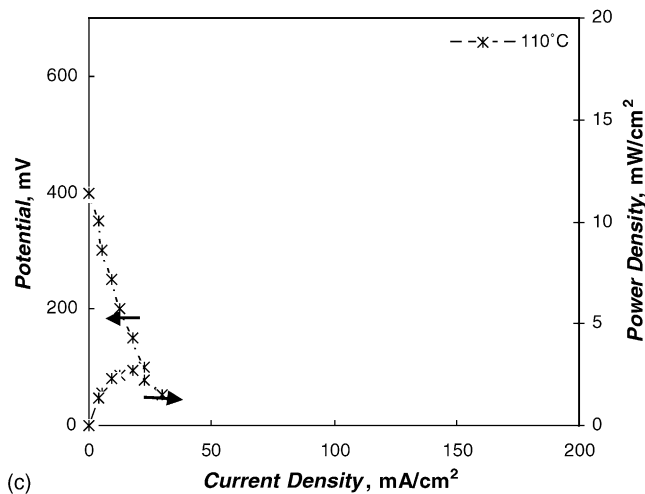
Analogous results were found for open-circuit voltage (OCV) experiments in terms of NPAI (Fig. 4a) and CO<sub>2</sub> concentration at the cathode outlet (Fig. 4c). However, the open-circuit potential seems to show a maximum value for the hybrid membrane with 7.5 wt.% ZrO<sub>2</sub> (Fig. 4b). This should happen due to the direct relationship between OCV and the methanol crossover and membrane ohmic resistance [11,12]. During OCV experiments, the concentration of methanol at the anode–membrane interface is maximal because no methanol is being consumed (no current output). Consequently, the methanol crossover is higher due to a larger mass transfer gradient across the membrane, making the detrimental effect of the methanol crossover more noticeable for OCV experiments [36]. Thus, the 5.0 wt.% ZrO<sub>2</sub> membrane presents lower OCV than that of the 7.5 wt.% because it has a higher methanol crossover [33]. The OCV increase should continue for higher ZrO<sub>2</sub> contents. However, the measurements of the open-cell voltage cannot be con-



(a)



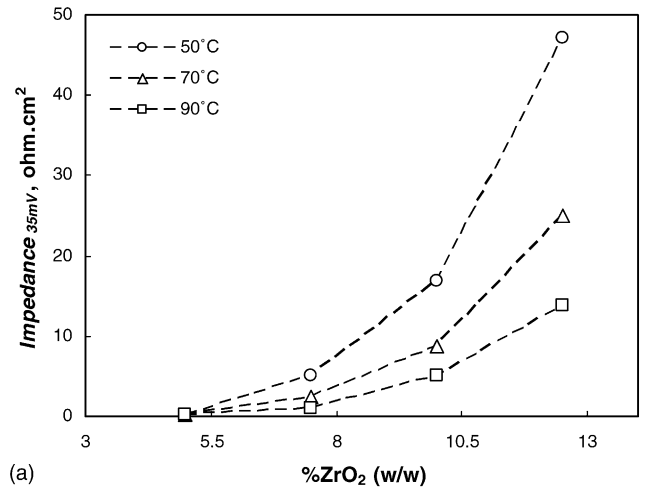
(b)



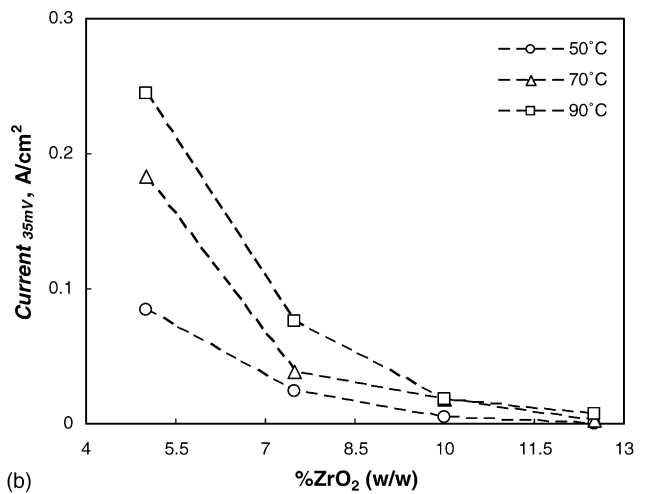
(c)

Fig. 2. Current–voltage and power density plots of the DMFC using sPEEK composite membranes with: (a) 5.0 wt.%, (b) 7.5 wt.% and (c) 10 wt.% ZrO<sub>2</sub>.

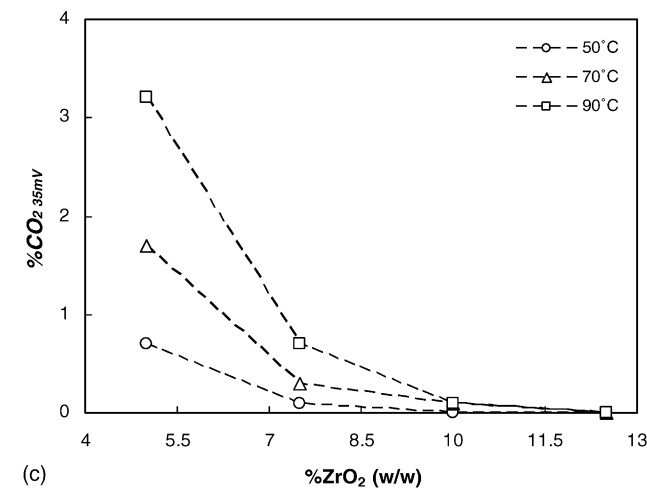
ducted without any cell current flowing. Because for both 10.0 and 12.5 wt.% ZrO<sub>2</sub> hybrid membranes, the ohmic resistance increases a lot with the amount of inorganic incorporation, the very small current flowing during the OCV measurement is



(a)



(b)



(c)

Fig. 3. Null phase angle impedance (a), current (b) and CO<sub>2</sub> concentration in the cathode outlet (c) for constant voltage DMFC experiments (35 mV) as a function of the ZrO<sub>2</sub> content.

sufficient to give a high voltage loss and consequently, OCV decreases.

In summary, from the DMFC characterization results it can be observed that even having a high methanol crossover

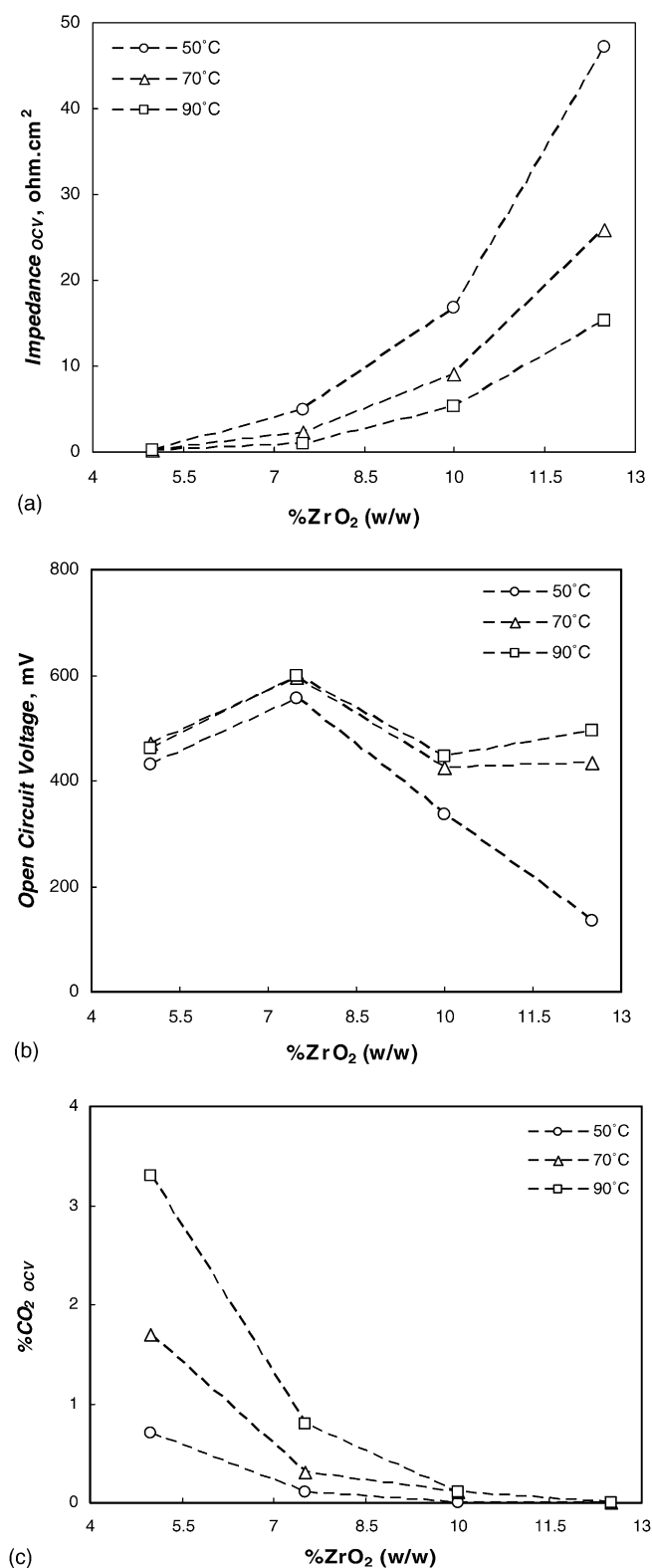


Fig. 4. Null phase angle impedance (a), current (b) and CO<sub>2</sub> concentration in the cathode outlet (c) for open-circuit DMFC experiments as a function of the ZrO<sub>2</sub> content.

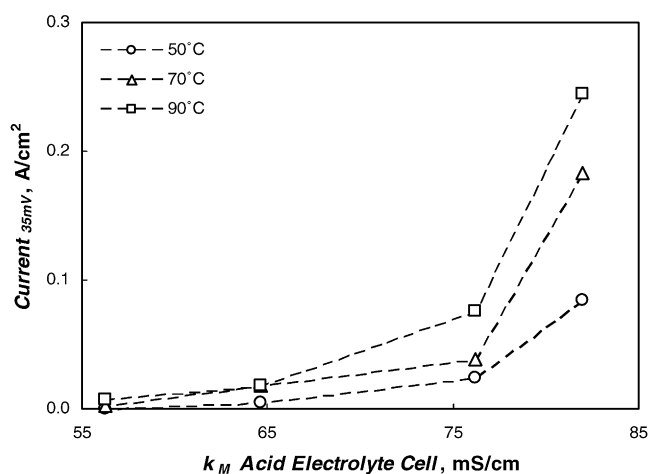


Fig. 5. DMFC current for constant voltage experiments (35 mV) as a function of proton conductivity evaluated in the acid electrolyte cell (25 °C).

and, consequently, higher CO<sub>2</sub> concentration in the cathode, the sPEEK inorganically modified membrane with 5.0 wt.% ZrO<sub>2</sub> presents the best DMFC performance among the studied membranes, in terms of output energy, mainly due to its high proton conductivity. However, as mentioned before, this membrane turned out to be the least stable one.

### 3.2. Membranes characterization results versus DMFC performance

In Fig. 5, the output current for CV experiments (35 mV) is plotted as a function of the proton conductivity, evaluated in the acid electrolyte cell (25 °C). It can be verified that for values lower than 75 mS cm<sup>-1</sup>, current increases slightly with proton conductivity. In comparison, higher values of proton conductivity lead to a strong increase in the DMFC current output (Fig. 5). In terms of the null phase angle impedance variation as a function of the proton transport resistance, evaluated in the acid electrolyte cell (Fig. 6), it seems that the DMFC resistance increases with the proton transport resistance, as expected. On the other hand, for the output current plot versus the membrane proton conductivity, evaluated in the cell using water vapour (Fig. 7), an analogous variation as noticed in Fig. 5 is observed for higher conductivities (strong current output increase), although the effect is not as pronounced as for the previous cell. Furthermore, for this cell the NPAI also increases with the proton transport resistance (Fig. 8). In general, the impedance spectroscopy in acid and vapour electrolytes seems to be a good criterion for selecting the right membranes for DMFC use. It seems that improved DMFC performance in terms of energy output occurs (current density) for conductivities above 75 and 20 mS cm<sup>-1</sup> in the acid and vapour electrolyte cells, respectively. For the studied membranes, proton conductivities lower than these values lead to poor DMFC performance.

In the particular case of the water uptake characterization method, Fig. 9 demonstrates that the electric current,

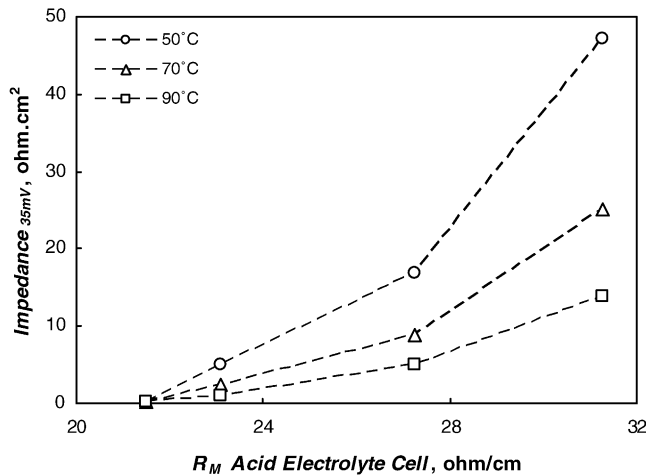


Fig. 6. DMFC null phase angle impedance for constant voltage experiments (35 mV) as a function of proton transport resistance evaluated in the acid electrolyte cell (25 °C).

for experiments performed at 35 mV, increases almost linearly with the water uptake (room temperature), showing that this characterization method is well related with such DMFC output. In contrast, the DMFC ohmic resistance seems to vary in a distinct way with the proton exchange membranes' water uptake (Fig. 9). Low values for the membrane water uptake result in a strong increase in the NPAI while higher amounts of sorbed water seem to affect slightly the ohmic resistance.

The carbon dioxide concentration at the cathode outlet was monitored as a measure of the methanol loss through the membrane during the fuel cell operation. Assuming that all methanol transferred to the cathode is oxidized to  $\text{CO}_2$ , the amount of methanol permeation can be calculated. This procedure neglects the unreacted methanol in the cathode (especially for lower temperatures) and the  $\text{CO}_2$  permeation through the membrane. The unreacted methanol in the cath-

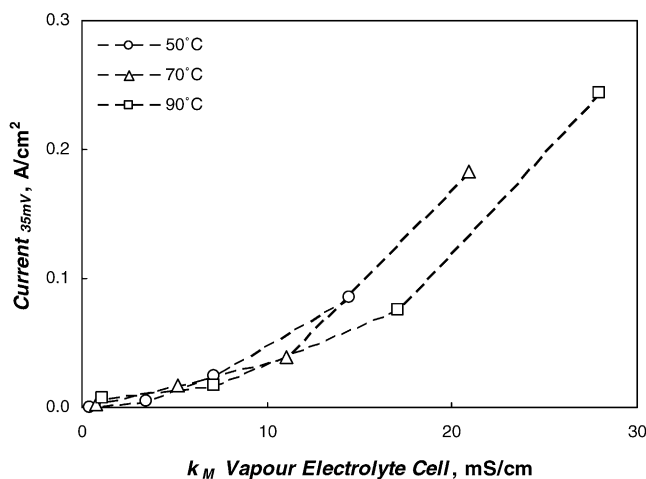


Fig. 7. DMFC current for constant voltage experiments (35 mV) as a function of proton conductivity evaluated in the vapour cell (50, 70 and 90 °C).

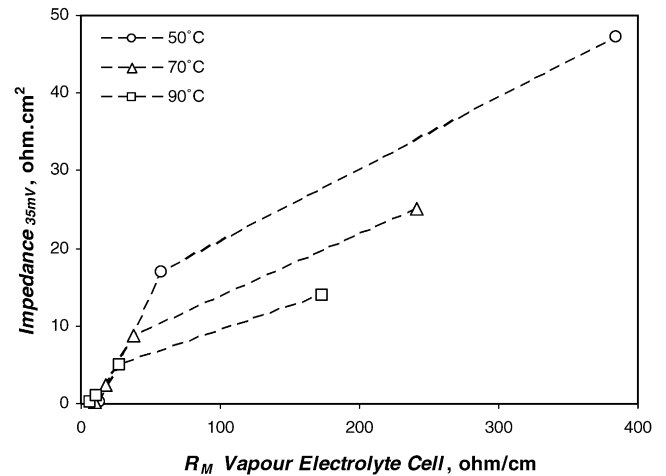


Fig. 8. DMFC null phase angle impedance for constant voltage experiments (35 mV) as a function of proton transport resistance evaluated in the vapour cell (50, 70 and 90 °C).

ode outlet would mean that the methanol permeation value calculated from the  $\text{CO}_2$  content would be too low. In contrast, the  $\text{CO}_2$  permeation from the anode to the cathode would mean higher concentrations of  $\text{CO}_2$  at the cathode outlet and, therefore, the calculated methanol permeation value would be too high. Even considering different membranes and using the same electrodes and the same operating conditions, the relative methanol permeation calculated from the  $\text{CO}_2$  content in the cathode outlet can be used for comparison.

Good agreement is found between the  $\text{CO}_2$  concentration in the cathode outlet and the water uptake (Fig. 10). The global analysis of these results shows the important role that sorbed water in the membrane plays in DMFC performance. It seems that sorbed water improves the DMFC energy output because it increases the membrane conductivity by assisting

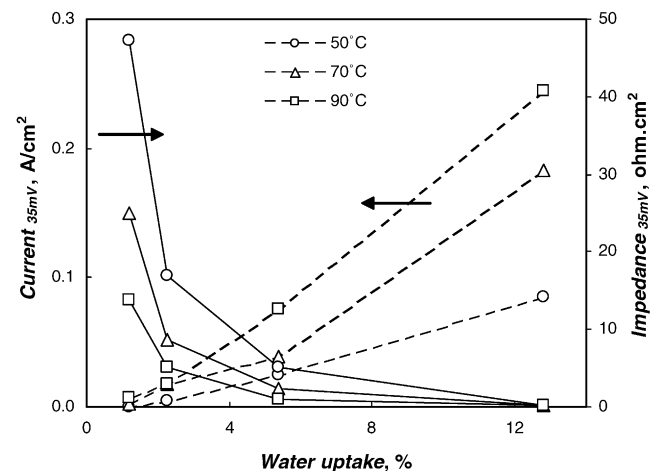


Fig. 9. DMFC current density and null phase angle impedance for constant voltage experiments (35 mV) as a function of water uptake evaluated by batch experiments (room temperature).

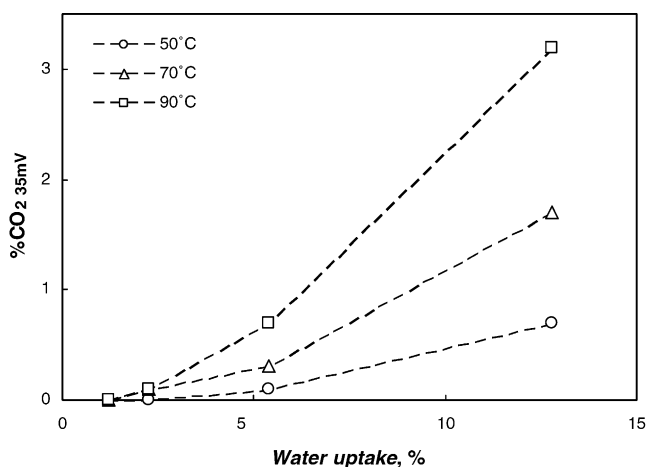


Fig. 10. Carbon dioxide concentration (%) in the cathode outlet for constant voltage experiments (35 mV) as a function of water uptake evaluated by batch experiments (room temperature).

the proton transfer in the polymer-hydrated microstructure [16]. However, it leads also to increased methanol crossover and, consequently, lower total efficiency with increased fuel loss and cathode depolarization [35–37].

Finally, in terms of the membrane permeability towards methanol, obtained by pervaporation experiments at 55 °C, it can be seen that it is in agreement with the CO<sub>2</sub> concentration in the cathode outlet (Fig. 11). For the lowest temperature (50 °C), it seems that the CO<sub>2</sub> concentration increases almost linearly with the methanol permeability coefficient. In contrast, for both 70 and 90 °C, the values for the highest methanol permeation are not as high as expected for a linear curve. This could mean that either the methanol transfer through the membrane is so high that it cannot be completely converted to CO<sub>2</sub>, or so much methanol is consumed in the

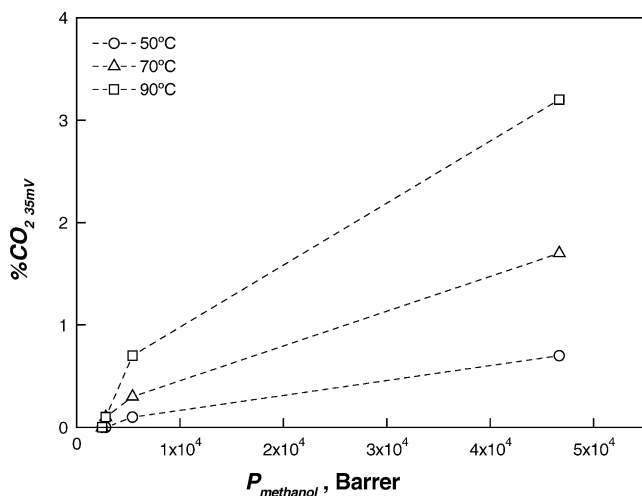


Fig. 11. Carbon dioxide concentration (%) in the cathode outlet for constant voltage experiments (35 mV) as a function of methanol permeability coefficient evaluated by pervaporation experiments (55 °C).

anode that the concentration gradient from anode to cathode and hence the methanol permeation are lower. In general, it can be assumed that even without accounting for the anode catalytic reaction and the electro-osmotic drag mass transfer, the permeability coefficients evaluated by pervaporation experiments are in good agreement with methanol crossover (Fig. 11).

As a whole, from the present study, it can be seen that characterization methods such as impedance spectroscopy, water uptake and pervaporation experiments can be used effectively for selecting the appropriate materials for DMFC application purposes and for estimating the fuel cell performance.

#### 4. Conclusions

In order to perform a critical analysis of the relationship between the results obtained from characterization methods and DMFC performance of a given electrolyte membrane, several hybrid membranes based on sPEEK polymer (S.D. = 87%) with different contents of zirconium oxide (5.0, 7.5, 10, 12.5 wt.%) were evaluated in a DMFC bench test. The selected characterization methods for the analysis were impedance spectroscopy (proton conductivity), pervaporation (permeability to methanol) and water swelling. The DMFC characterization consisted in investigating the current–voltage polarization curves, constant voltage current (CV, 35 mV), and open-circuit voltage (OCV).

The results showed that increasing the zirconium oxide content in the sPEEK composite membranes leads to a decrease in the DMFC current density for CV experiments, CO<sub>2</sub> concentration at the cathode exhaust for both OCV and CV experiments and, finally, maximum power density output. The opposite effect was verified in terms of the NPAI (ohmic resistance). Bench test results showed also that the sPEEK-based hybrid membrane with 7.5 wt.% ZrO<sub>2</sub> presents the highest open-circuit potential due to its better ratio between methanol crossover and ohmic resistance in comparison with the other studied membranes. With respect to the validation of the characterization methods, results showed a co-current variation between proton conductivity, evaluated by impedance spectroscopy (acid electrolyte and water vapour cells), and DMFC output current density. The same behavior was observed regarding the proton transport resistance, evaluated in characterization cells, and the DMFC null phase angle impedance for CV experiments. A strong increase of the output current density for conductivities higher than 75 and 20 mS cm<sup>-1</sup> was found in the acid electrolyte and vapour cells, respectively. On the other hand, an almost linear variation was detected between the water uptake and the DMFC output current density for CV experiments. The fuel cell ohmic resistance seems to increase strongly for membranes with low water uptake, while it is almost independent for higher values of this property. Finally, our results showed a good agreement between the membranes' methanol permeability coefficients obtained by pervapora-

tion experiments and the CO<sub>2</sub> concentration in the cathode outlet.

The present publication shows that characterization results obtained by impedance spectroscopy, water uptake and pervaporation experiments can be used as critical parameters for the selection of proton electrolyte membranes for DMFC application purposes.

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