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Non-Fluorinated Membranes Thickness Effect on the DMFC Performance

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Abstract: In order to study the influence of the proton exchange membrane thickness on the direct methanol fuel cell (DMFC) performance, sulfonated poly (ether ether ketone) (sPEEK) membranes with a sulfonation degree (SD) of 42% and thicknesses of 25, 40, and 55 μm were prepared, characterized, and tested in a DMFC. These polymeric membranes were tested in a DMFC at several temperatures by evaluating the current-voltage polarization curve, the open circuit voltage (OCV) and the constant voltage current (CV, 35 mV). The CO_2 concentration at the cathode outlet was also measured. The thinnest sPEEK membrane proved to have the best DMFC performance, although having lower Faraday efficiency (lower ohmic losses but higher methanol permeation). In contrast, the thickest membrane presented improved properties in terms of methanol permeation (lower methanol crossover). DMFC tests results for this membrane showed 30% global efficiency, obtained with pure oxygen at the cathode feed.

Keywords: Direct methanol fuel cells; Pervaporation; Proton conductivity; Sulfonated poly(ether ether ketone) (sPEEK); Thickness

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INTRODUCTION

Direct Methanol Fuel Cells (DMFCs) arise from the fuel cells technology as one of the most interesting ones, which relevance is growing considerably. The basic operation principle of a DMFC is schematically shown in Fig. 1, which illustrates the species mass transport trough the proton exchange membrane. The involved reactions in the DMFC are the following:

$$\text{Anode reaction: } CH_3OH + H_2O \xrightarrow{Pt/Ru} CO_2 + 6H^+ + 6e^- \quad (1)$$

$$\text{Cathode reaction: } \frac{3}{2}O_2 + 6H^+ + 6e^- \xrightarrow{Pt} 3H_2O \quad (2)$$

$$\text{Overall reaction: } CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \quad (3)$$

One of the main DMFC development challenges is to reduce the water and methanol crossover from the anode to the cathode without affecting the proton conductivity (1). Methanol crossover is intimately related with a number of factors, namely the operating temperature, anode performance, concentration of the feed aqueous solution of methanol, and the membrane permeability and thickness (2). Because water and methanol molecules are similar, there is always some methanol crossing directly from the anode to the cathode, due to molecular diffusion and electro-osmotic

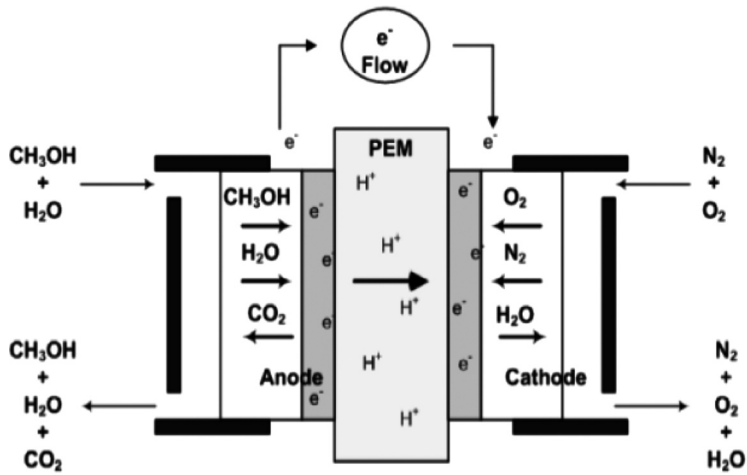


Figure 1. Sketch of a DMFC illustrating water, methanol and protons transport through the proton exchange membrane.

drag, without producing electrical power. Molecular diffusion is more relevant at low current densities and electro-osmotic drag plays a crucial role at high current densities (3).

The methanol crossover not only lowers the fuel utilization but also causes the cathode depolarization (1,4–5). On the other hand, excessive water permeation is also detrimental for DMFC performance because it causes cathode flooding, resulting in a significant performance loss (6). Jung et al. analyzed the weight percentage of methanol remaining in the drain water coming out from the cathode and verified that with Nafion® 112 this concentration was three times higher than with Nafion® 117 (50 μm and 180 μm membrane thickness, respectively) (7). Thus, the increase of the proton exchange membranes thickness can decrease the reactants loss during DMFC operation, improving the overall fuel conversion performance. Furthermore, the mechanical stability of the membrane might also be improved, providing long-term structural integrity for the fuel cell practical use. In the particular case of Nafion®, it seems that 50 μm is the minimum thickness for the necessary mechanical stability (6). In contrast with the benefits mentioned before, the proton transport resistance increases with the membrane thickness (6). Thinner membranes show lower resistance in the cell because the protons' overall pathway to cross from the anode to the cathode is also smaller (6). On the other hand, reduced thickness leads to a faster hydration of the PEM and also to a lower cost.

Therefore, the membrane thickness has to be selected carefully in order to achieve a compromise between different requirements (8); the optimum thickness should enable a good balance between high proton conductivity, good chemical stability, low water and methanol permeabilities, high water/methanol selectivity, and low cost of the membrane.

In order to evaluate the influence of the thickness of sulfonated poly(ether ether ketone) membranes (sPEEK) on the fuel cell performance, we synthesized, characterized, and applied pure sPEEK membranes in a DMFC system. The characterized properties were the specific proton transport resistance and methanol permeation fluxes. In terms of the DMFC test, we have measured the current-voltage polarization curves, the constant voltage current (CV, 35 mV), and the open circuit voltage (OCV). The CO_2 concentration at the cathode outlet was also monitored as a measure of the methanol crossover during DMFC operation (1).

EXPERIMENTAL

Materials and Methods

Poly(ether ether ketone) (PEEK) was supplied as pellets by Victrex and sulfonated in our laboratories as described in the literature (9). The final

sulfonation degree obtained was 42% (ion exchange capacity of 1.27 meq/g). The sulfonation degree was determined by elemental analysis and by H-NMR.

Membrane Preparation

In order to prepare membranes with different thicknesses, the sPEEK polymer was dissolved in dimethylsulfoxide at concentrations of 4, 5, and 6 wt.% and left to stir for one day. The final pure sPEEK solutions were cast in a hydrophobized glass plate heated at 70°C. After casting, the membranes were stored in a vacuum oven for 24 hours at 90°C. Membrane thickness was measured using a micrometer, from TESA Micromaster.

The hydrophobized glass plate was prepared by introducing a glass plate in a 2 wt.% NaOH aqueous solution for 2 days, washed afterwards with distilled water and dried with a tissue. After, the silanization solution (1000 ml of chloroform, 30 ml of octadecyl triethoxy silane, and 1 ml of triethyl amine) was applied to the dry plate. After 30 minutes the plate was washed again with distilled water and dried in a vacuum oven for 2 hours at 70°C.

Membrane Characterization Methods

Proton Transport Resistance

Specific resistance (proton transport resistance per membrane area) measurements were carried out at 25°C in a cell described elsewhere (10), filled with 0.33 M sulfuric acid to improve the electrical connection between the electrodes and the membrane, using ac impedance spectroscopy. The proton transport resistance is obtained from the high frequency interception with the real axis of the Nyquist plot. A membrane sample was placed in the sulfuric acid solution between two platinum electrodes, 2.8 cm in diameter and distancing about 2 mm from each other. Samples were pre-treated by immersion in water at room temperature during 3 days to ensure total leaching. Additionally, one hour before the measurement the samples were immersed in the electrolyte solution. The spectrometer used was a HP 4284 A, working in the frequency range between 100 and 10^5 Hz.

Methanol Permeation Fluxes

The methanol permeation fluxes were evaluated through pervaporation as described in (11). The pervaporation experiments consist on measuring

the amount of permeated methanol and water through a membrane during a certain period of time. During the experimentation, the permeate was collected in a glass U-shaped tube immersed in liquid nitrogen inside a Dewar flask. The pervaporation experiments lasted between 2 to 3 hours. At the end the collected permeate was liquefied, weighted, and the methanol concentration evaluated using a refractometer. The measurements were performed at 40, 55, and 70°C with a 6.0 M aqueous methanol solution (20 wt.%). The pervaporation set-up is described elsewhere (11). Prior to all measurements, samples were immersed in the feed solution for 1 hour.

DMFC Tests

The membrane electrode assemblies (MEAs) were prepared by hot pressing the membrane samples between two Etek® ELAT electrodes. Supported PtRu (1 mg/cm^2, 30 wt.% PtRu(1:1) on carbon with 0.7 mg/cm^2, Nafion®/PTFE) and Pt (0.4 mg/cm^2, 20 wt.% Pt on carbon with 0.7 mg/cm^2, Nafion®/PTFE) were used as anode and cathode electrodes, respectively. The DMFC experimental set-up is described elsewhere (12). The MEAs (25 cm^2) were fed with an aqueous 1.5 M methanol solution (4 ml/min, 2.5 bar) to the anode side and humidified air (600 sccm/min, 3 bar, 100% relative humidity) to the cathode side. Though, the efficiency tests were performed with a 0.5 M aqueous methanol feed stream and with the thickest sPEEK membrane (55 μm). The MEAs' characterization was performed measuring the DMFC current-voltage polarization curves, constant voltage current (CV, 35 mV), and open circuit voltage (OCV). The last two parameters investigated also included the measurement of the CO_2 concentration at the cathode outlet. Data acquisition began after 2 hours of commissioning at 22°C. The DMFC efficiency was evaluated as described in (13). Basically, the potential efficiency is defined as the DMFC voltage divided by the standard cell voltage. On the other hand, the Faraday efficiency is defined as the ratio between the converted fuel for current production (anode) and the total amount of converted fuel (anode and cathode). The DMFC global efficiency was obtained combining both Faraday and potential efficiencies.

RESULTS AND DISCUSSION

Characterization Results

The proton exchange membrane plays a crucial role on the DMFC operation, preventing the reactants loss as well as electricity crossover, and

Table 1. Proton transport resistance, per unit of membrane area, and methanol flux of the sPEEK membranes with different thickness

		Methanol Flux* ($g\,h^{-1}\,m^{-2}$)		
Membrane Thickness (mm)	R_M (Ω/cm^2)	40°C	55°C	70°C
0.025	4.17	146.2	622.4	925.6
0.040	6.07	97.0	406.7	796.9
0.055	8.00	92.2	398.0	742.9

*Feed pressure 1 bar and vacuum in the permeate side.

ensuring low protons resistance between the anode and the cathode. From Table 1 it can be seen that the proton resistance, per unit of membrane area, increases with the membrane thickness. The methanol permeation fluxes for the analyzed sPEEK membranes are also given in Table 1. The methanol crossover flux decreases with the membrane thickness. On the other hand, it can also be seen that methanol fluxes increase with temperature for all the studied thicknesses. The proton conductivity/methanol permeability selectivity (β) allows to compare the different sPEEK membranes and to point out the combined effect of the membrane thickness. Figure 2 plots the logarithm of β as a function of the membrane thicknesses for 40, 55, and 70°C. There is no clear trend

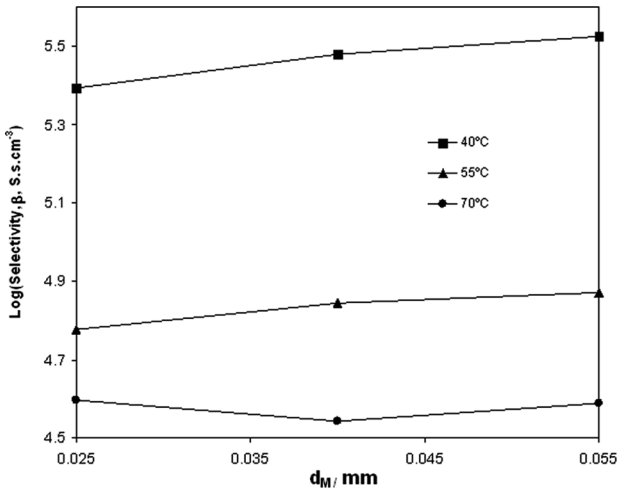


Figure 2. Proton conductivity (evaluated at 25°C)/methanol permeability selectivity of sPEEK (SD = 42%) membranes as a function of the membrane thickness at 40, 55 and 70°C.

pointing out the best combination between proton conductivity and methanol permeability. Indeed, the differences found on the data are practically within the experimental error, which were computed based on the average error for each of the techniques: 5.5% and 4.7% (t-distribution, 95% confidence interval) for the proton conductivity and methanol permeability, respectively. In summary, it can be concluded that the selectivity is nearly constant independently of the tested temperatures, on the studied thickness range. Moreover, it was observed that for sPEEK membranes with sulfonation degrees between 71 and 87%, the membrane swelling is approximately independent of its thickness (14) and the same should be hold for the present membrane.

DMFC Results

The current density-voltage and current density-power density plots of the MEAs produced with the sPEEK membranes at different temperatures are shown in Fig. 3. From this figure it can be seen that the membrane performance, in terms of power output, decreases with the membrane thickness. We believe that the performance of a fuel cell concerning membranes with different thicknesses is intimately related with the combined effect of ionic conductivity and permeation of methanol from the anode to the cathode. Although having higher permeation of methanol (lower fuel conversion), the fuel cell power output is higher for thinner membranes due to reduced ohmic losses.

From Fig. 4, one can observe that the open circuit voltage increases with thickness. As it is known, the DMFC open circuit voltage is well related with the methanol parasitic polarization (7). For thinner membranes higher flow rates of methanol from the anode to the cathode are expected, and therefore, higher voltage losses.

In terms of the carbon dioxide concentration at the cathode exhaust for open circuit experiments (measure of the methanol crossover), one can observe, from Fig. 5, that the CO_2 concentration at the cathode exhaust decreases with the membrane thickness, which is related with the decreased methanol permeation. It can be also seen that, for all membranes, the amount of CO_2 produced at the cathode increases with temperature. The last feature happens essentially because the mechanism associated to methanol crossover at open circuit conditions is the molecular diffusion and it is well known that the methanol diffusion rate increases with temperature. On the other hand, once methanol is not consumed at the anode side (OCV conditions), the reaction rate regarding its conversion into carbon dioxide at the cathode Pt sites is also favoured by a higher temperature.

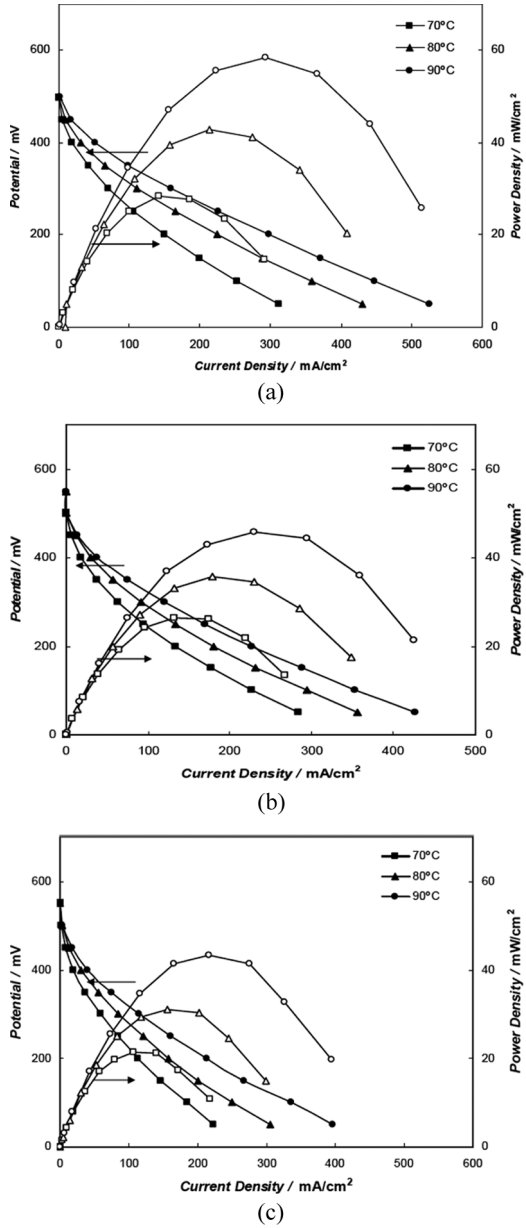


Figure 3. Current density-voltage and current density-power density plots of the DMFC using sPEEK (SD = 42%) membranes with thicknesses: a) 0.025, b) 0.040 and c) 0.055 mm.

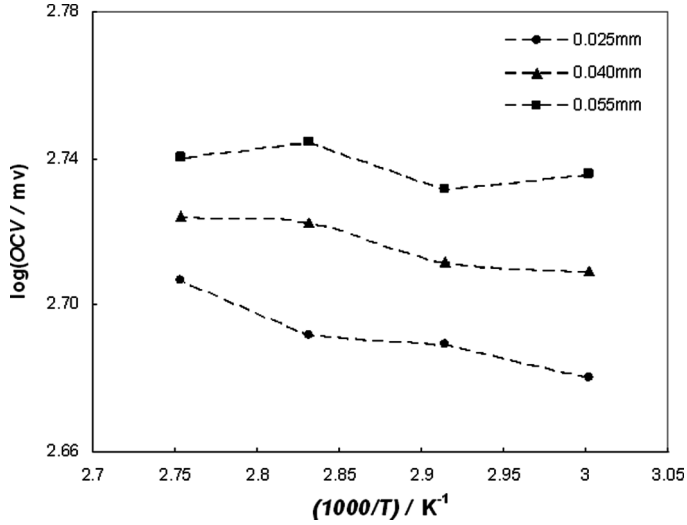


Figure 4. Open circuit voltage as a function of temperature for the DMFC using sPEEK (SD = 42%) membranes with different thicknesses.

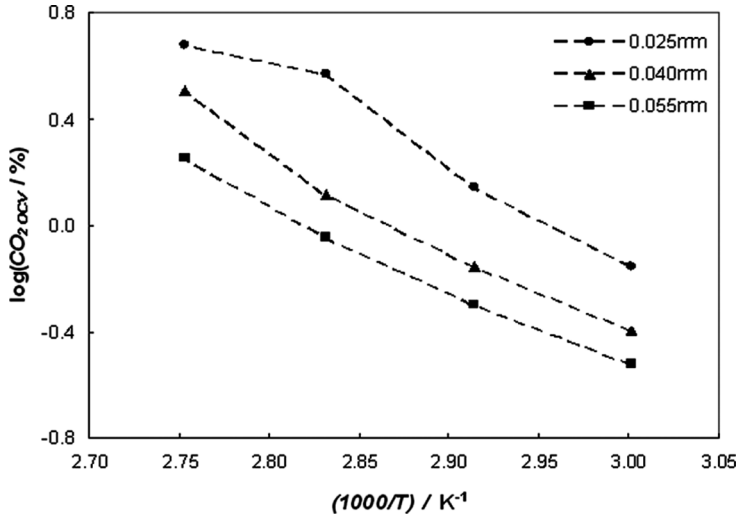


Figure 5. CO_2 concentration at the cathode outlet as a function of temperature for open circuit DMFC experiments using sPEEK (SD = 42%) membranes with different thicknesses.

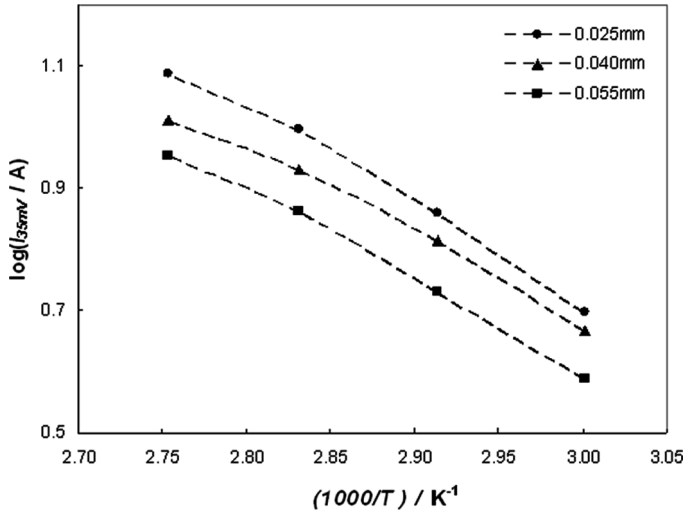


Figure 6. Current output (constant voltage experiments at 35 mV) as a function of temperature for the DMFC using sPEEK (SD = 42%) membranes with different thicknesses.

Figure 6 shows the fuel cell current output at 35 mV as a function of the membrane thickness and DMFC operation temperature. As expected, the highest values of the current are obtained for the membrane with lower thickness due to lower ohmic losses. The current output increases with the temperature and decreases with the membrane thickness. At low voltage, the decrease of the membrane thickness leads to the reduction of charge transfer resistance from the anode to the cathode side.

For 35 mV experiments, the CO_2 concentration at the cathode exhaust (Fig. 7) is lower than that for the open circuit voltage conditions (Fig. 5). Under load, there is a lower methanol mass transfer gradient across the membrane because methanol is reacting, leading to a reduction of its concentration in the vicinity of the membrane. Consequently, methanol permeation is more noticeable for open circuit experiments. Once again, carbon dioxide concentration increases with the DMFC operating temperature but decreases significantly when thicker membranes are employed (Fig. 7).

Figure 8 shows that higher Faraday efficiencies (measure of the methanol conversion) are obtained for thicker membranes due to higher barrier properties. As the DMFC temperature increases, the Faraday efficiency decreases which evidences the more relevant role of methanol permeation. In terms of the power density output, the reverse trend is observed. In other words, the membrane thickness is one of the key factors that should be selected according to the DMFC application

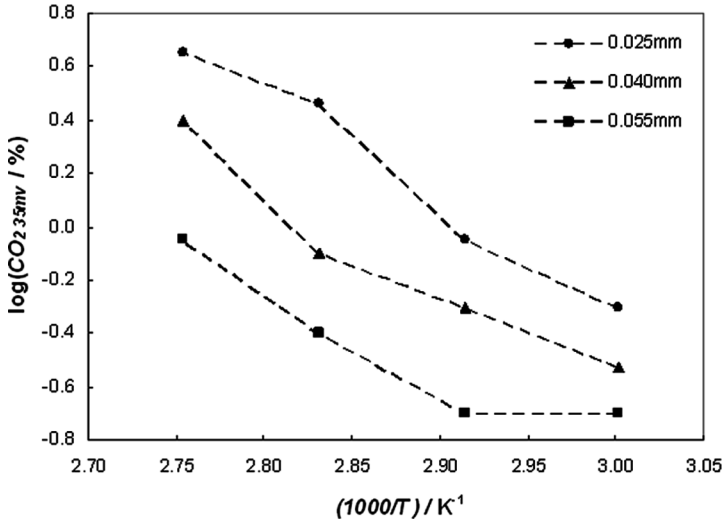


Figure 7. CO_2 concentration at the cathode outlet as a function of temperature for constant voltage DMFC experiments (35 mV) using sPEEK (SD = 42%) membranes with different thicknesses.

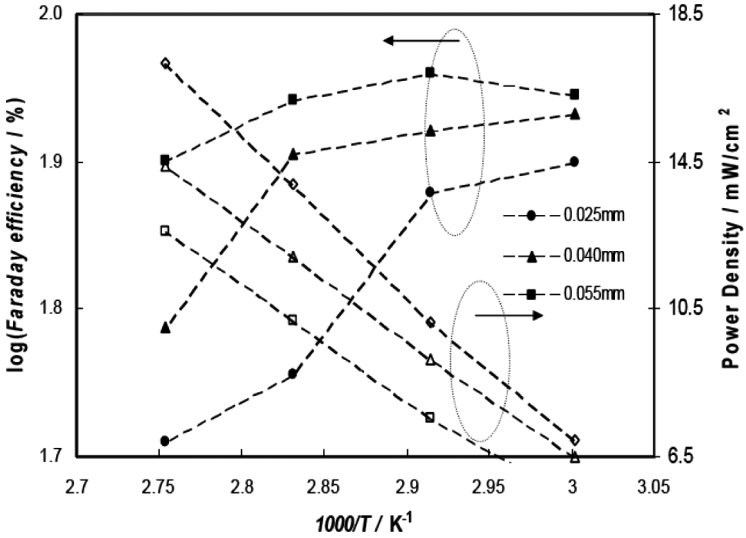


Figure 8. Faraday efficiency and power density (constant voltage experiments at 35 mV) as a function of temperature for the DMFC using sPEEK (SD = 42%) membranes with different thicknesses.

needs; higher power density production or higher Faraday efficiency. The choice of membrane thickness is not a simple question and should always be pointed out regarding the application. The development of thinner membranes, able to combine improved efficiencies with high power densities, will be a very important technological jump.

Figure 9 plots the OCV (a) and current density (b) histories after changing the DMFC load from 35 mV to open circuit and from open circuit to

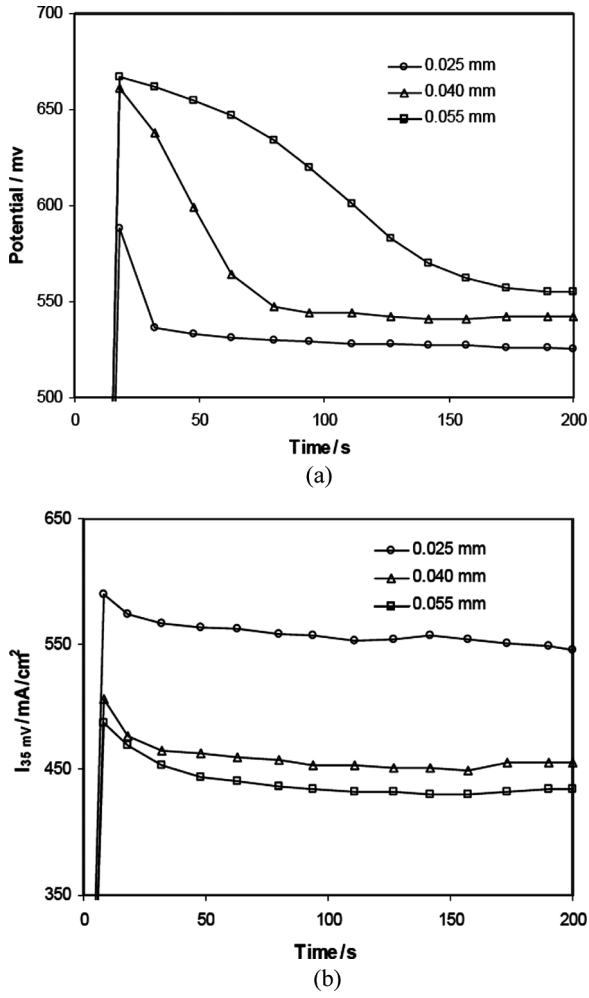
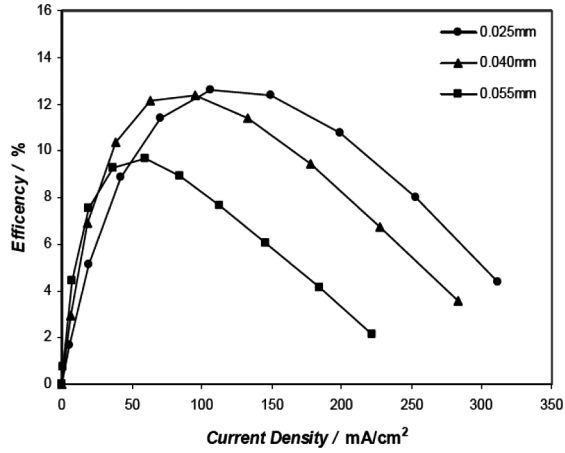
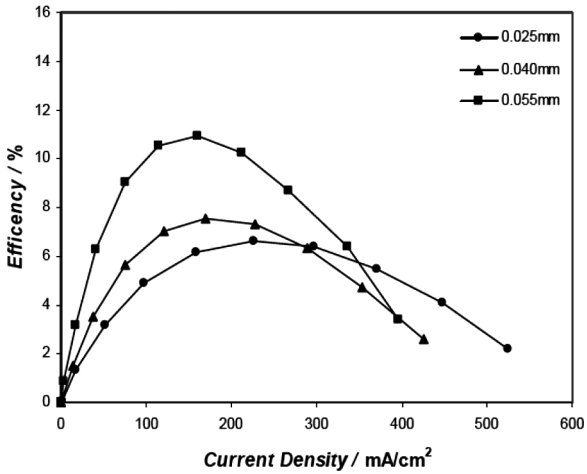


Figure 9. Open circuit voltage (a) and current density (b) as a function of time during the response to a step perturbation on the DMFC at 90°C from 35 mV to open circuit and from open circuit to 35 mV, respectively. Lines are there for easy reading.



(a)



(b)

Figure 10. Estimated efficiency of the DMFC as a function of current density, using sPEEK (SD = 42%) membranes with different thicknesses and at different temperatures: (a) 70°C, (b) 90°C.

35 mV, respectively. When changing from 35 mV to open circuit, it is seen that the OCV increases abruptly and reaches a peak for all the studied membranes. This behavior is intimately related with fuel cell ohmic losses. On the other hand, rather than stabilizing at this voltage, the OCV starts to decay over time, assuming a behavior which is related with reaction kinetics and mass transport processes, namely the mass transfer of methanol through the membrane (15). The thicker the membrane, the more

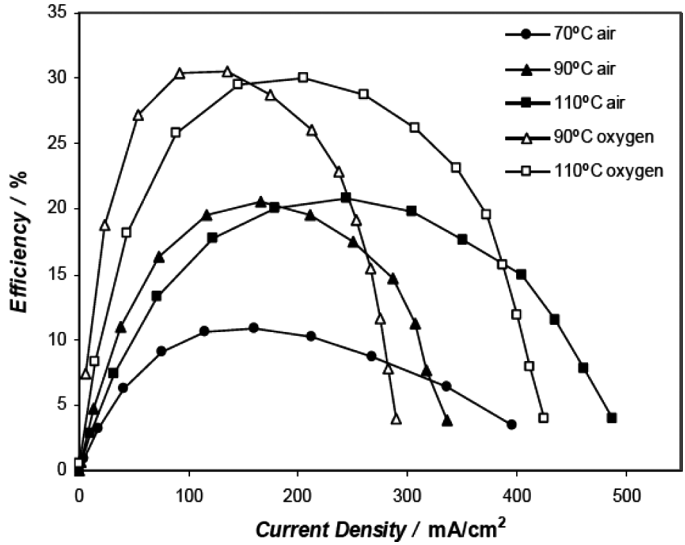


Figure 11. Estimated efficiency of the DMFC as a function of the current density, using the sPEEK (SD = 42%) membrane with a thickness of 0.055 mm.

time is required for OCV stabilization, and also the higher the final OCV value, in agreement with the trends shown before (Fig. 4). At high current densities (35 mV), methanol is reacting at the anode catalyst layer leading to lower methanol concentrations and consequently less methanol crosses the membrane. After the load cut, the methanol concentration at the anode starts to increase, leading to a higher value of methanol crossover. As a consequence, the methanol concentration also increases at the cathode and the voltage starts to decrease (methanol crossover). Differences of more than 0.1 V are found between the peak and the plateau voltages after the perturbation from 35 mV to OCV – Fig. 9a. However, thinner membranes respond faster due to smaller diffusion constant times. From Fig. 9b it can be seen that the change from OCV to a stabilized current density at 35 mV occurs in a shorter period of time for all studied membranes. Shorter relaxation times were observed when the system is perturbed from OCV to 35 mV then the other way round – Fig. 9. Once again, thinner membranes have a slightly faster stabilization. This is an advantage when fast load responses are required which is the case, for example, when fuel cells are used to supply power to transportation vehicles.

In Fig. 10 is plotted the computed overall efficiency of the DMFC using sPEEK membranes with different thickness, at 70°C (a) and 90°C (b), as a function of the current density. From the 70°C plots, Fig. 10a, one can observe that the thinnest membrane, although with lower

efficiency for lower current density (less than 50 mA/cm^2), presents the highest efficiency for higher current densities (enhanced proton conductivity is the main factor in this region). In contrast, at 90°C, the same trend is observed but only after ca. 350 mA/cm^2. When increasing the temperature, methanol permeation from the anode to the cathode also increases and becomes the most relevant effect in a higher range of current densities. Only after that point (i.e. ca. 350 mA/cm^2), the thinnest membrane has higher efficiency.

Therefore, we performed further DMFC tests using the thickest sPEEK membrane, i.e., with a thickness of 0.055 mm, this time at a lower methanol concentration, 0.5 M – Fig. 11. From these tests we were able to reach fuel cell efficiencies near 30% using pure oxygen as oxidant at the cathode, which is quite good for DMFC.

CONCLUSIONS

The study performed shows that the membrane thickness has high influence on the proton transport resistance and methanol permeation. Thinner membranes have lower proton resistance and higher methanol permeation. The DMFC tests results showed the same trend. Higher current densities and power densities were obtained for thinner membranes (lower ohmic losses). For thinner membranes, the decreased concentration of methanol at the anode catalyst layer for high current densities decreased the detrimental methanol polarization effect at the cathode, improving the DMFC efficiency and power output. However, the thickest membrane proved to have higher overall efficiency at higher temperatures due to lower methanol loss. At 90 and 110°C, this membrane provided overall efficiencies near 30% using pure oxygen at the cathode feed. Thinner membranes also showed a faster dynamic response to load changes, namely from 35 mV to open circuit and from open circuit to 35 mV, due to faster mass transfer kinetics.

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