Journal of Power Sources 195 (2010) 4036–4042

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Modified SPEEK membranes for direct ethanol fuel cell

Husnul Maab [1], Suzana Pereira Nunes *

GKSS Research Centre Geesthacht GmbH, 21502 Geesthacht, Germany

ARTICLE INFO

Article history:
Received 2 October 2009
Received in revised form
16 December 2009
Accepted 3 January 2010
Available online 25 January 2010

Keywords:
DEFC
DAFC
Fuel cell
Membrane
Polyimide
SPEEK

ABSTRACT

Membranes with low ethanol crossover were prepared aiming their application for direct ethanol fuel cell (DEFC). They were based on (1) sulfonated poly(ether ether ketone) (SPEEK) coated with carbon molecular sieves (CMS) and (2) on SPEEK/PI homogeneous blends. The membranes were characterized concerning their water and ethanol solution uptake, water and ethanol permeability in pervaporation experiments and their performance in DEFC tests. The ethanol permeabilities for the CMS-coated (180 nm and 400 nm thick layers) SPEEK were 8.5 and 3.1×10^{-10} kg m s^{-1} m^{-2} and for the homogeneous SPEEK/PI blends membranes with 10, 20 and 30 wt.% of PI were 4.4, 1.0 and 0.4×10^{-10} kg m s^{-1} m^{-2} respectively, which is 2- to 50-fold lower than that for plain SPEEK (19×10^{-10} kg m s^{-1} m^{-2}). Particularly the SPEEK/PI membranes had substantially better performance than Nafion 117® membranes in DEFC tests at 60 °C and 90 °C.

1. Introduction

Among various types of fuel cell, the direct alcohol fuel cell (DAFC) has been seen for many years as the best candidate to open the early market for the fuel cell technology. The reason for that is that when working with liquid fuels the delivery infrastructure would be already available and the additional problems of storage, exceptional safety issues and eventual on-board fuel production, which are known for hydrogen, would be minimum in the case of alcohol. In the last decade the efforts of groups all over the world have been concentrated on direct methanol fuel cells, since the catalytic reaction of methanol to supply protons is much easier. However ethanol would be much more interesting as a fuel, because of its non-toxic nature and higher theoretical energy density of (8 kW h kg^{-1}), compared to that of methanol (6 kW h kg^{-1}). Direct ethanol fuel cells (DEFC) are promised as a power supply for stationary and portable devices. DEFC in the form of micro-fuel cell can be a good alternative for the lithium-ion secondary batteries. Moreover ethanol, being a renewable bio-fuel, can be produced in large volume by the fermentation of biomass or common crops like sugar cane and corn through a simple manufacturing process. The top five ethanol producers in 2006 were USA, Brazil, China, India and France but USA and Brazil accounted for 70% of the total ethanol production worldwide of 13.5 billions US gallons (40 millions tons). While in 2007 the share of USA and Brazil towards the production of fuel ethanol increased up to 88% of the total world production of 13.1 billions US gallons. Ethanol is considered as an alternative to gasoline in some parts of the world contributing to a clean environment with a better opportunity for life standard [1–3].

The main hurdle for the success of direct ethanol fuel cell is still the lack of high performance catalysts and membranes. From the literature survey it is evident that much more work is focused on the development of different kind of catalysts for the complete oxidation of ethanol (breaking of C–C bond in addition with C–H and O–H bonds) without producing acetic acid, acetaldehyde etc. with the removal of all 12 electrons [1–10]. Many kinds of polymeric membranes were tested with direct methanol fuel cell (DMFC) since 1960 and they can now be testified for DEFC. The main objective is also how to achieve high proton conductivity with low fuel crossover through the membrane. Sulfonated poly(ether ether ketone) (SPEEK) based composite with functionalized inorganic silanes and a blend of silica with sulfonated poly(oxy-1,4-phenyleneoxy-1,4 phenylenecarbonyl-1,4 phenylene), (SPEEK) and (PES) [10–12] were reported for the low ethanol crossover during DEFC application. A simulation study was carried out to determine the ethanol crossover through the Nafion® membranes in terms of different operating temperatures and with different ethanol concentrations [13].

In this paper, membranes made of SPEEK coated with carbon molecular sieves (CMS) with different thickness layers and SPEEK

* Corresponding author at: 4700 King Abdullah University of Science and Technology, Membranes Research Center, KAUST, Thuwal 23955-6900, PO Box 2083, Saudi Arabia. Tel.: +966 2 8082771; fax: +966 2 8082771.
E-mail address: suzana.nunes@kaust.edu.sa (S.P. Nunes).
[1] Current address: National Engineering and Scientific Commission (NESCOM), PO Box 2216, Islamabad, Pakistan.

0378-7753/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2010.01.005

blended with polyimide (PI) in different concentration ratios are reported. The idea of preparing and using thin layer of CMS is to take advantage of its nano-porous structure for stopping alcohols crossover during fuel cell performance. The fuel crossover in membranes prepared from blends of polyimide (PI) and SPEEK can be reduced, by using the advantage of PI hydrophobicity. The performances of analogous membranes in DMFC have been recently published by our group [14,15]. Now the CMS-coated SPEEK bilayer membranes and SPEEK/PI blend membranes were characterized aiming application in DEFC. The DEFC performance and ethanol crossover results are reported here.

2. Experimental

2.1. Materials

Matrimid® 5218, a polyimide produced by the condensation of 3,3,4,4-benzophenone tetracarboxylic dianhydride and diaminophenylindane, commercialized by Ciba Geigy (Switzerland), was the precursor for the carbon molecular sieve (CMS) layer used in the bilayer membrane and also the polyimide chosen for the SPEEK/PI blend membrane preparation. The polymer was heated in an oven at 120 °C for 24 h to remove any residual water before starting the membrane preparation.

Sulfonated poly(ether ether ketone) (SPEEK) was prepared by sulfonation of poly(ether ether ketone), purchased from VICTREX, which was dried at 120 °C under vacuum and reacted according to procedures reported before [16]. Chloroform (99.0–99.4%), dimethyl sulphoxide (DMSO) (99.9%) and ethanol (99.9%) were purchased from Merck and used as received.

Nafion 117® was bought from Du Pont.

The fuel cell electrodes and diffusion layers were purchased from E-Tek (BASF). The cathode electrodes were loaded with 100% platinum black catalyst (4 mg cm^{-2}) and the anode material was loaded with 60% of Pt:Ru (3 mg cm^{-2}). Both electrodes were prepared on Vulcan X-72.

2.2. Preparation of membranes

2.2.1. CMS-SPEEK membranes

The CMS-coated SPEEK membranes were prepared according to procedure reported before [14]. Matrimid® 5218 solutions in chloroform with different concentrations were cast on quartz plates and pyrolyzed to form 180 nm and 400 nm CMS layers. The layers were coated with SPEEK solution. After solvent evaporation, the bilayer membrane was detached from the quartz substrate.

2.2.2. SPEEK/PI blend membranes

For the preparation of SPEEK/PI blends, SPEEK (degree of sulfonation DS 56%) and polyimide (10, 20 and 30 wt.%) were dissolved in DMSO. The solution was stirred at *t* 130 °C for 24 h. After the mixing step, SPEEK/PI films were prepared by casting the homogeneous polymer solution on clean glass plates, which were then heated at 100 °C for 24 h, followed by an additional 24 h at 100 °C in vacuum oven in order to eliminate any rest of solvent. The films were easily detached from the glass and were immersed in de-ionised water. Membranes were then obtained with the following polymer weight ratios: SPEEK/PI blend (90/10), SPEEK/PI blend (80/20), SPEEK/PI blend (70/30).

2.3. Morphology

The morphology of the CMS-coated SPEEK bilayer membrane and the SPEEK/PI dense films were studied by scanning electron microscopy (SEM) using a LEO 1550 VP field emission microscope. The samples were prepared by fracturing the films in liquid nitrogen and coating them with Au/Pd by sputtering.

2.4. Water and alcohol uptake

The uptake of de-ionised water and 5 wt.% ethanol aqueous solutions by Nafion 117®, plain SPEEK and SPEEK/PI membranes was measured at room temperature (25 °C) and at 60 °C. All the membranes were dried in a vacuum oven at 120 °C for 24 h.

3.0 cm × 3.0 cm films were weighed and then immersed in de-ionised water and in 5 wt.% ethanol solution for 24 h. After that, and before weighting again, the excess water was quickly removed with tissue paper. The measurements were repeated three times and the results reported are the average values. The water and ethanol/water solution uptake values were calculated according to the following equation:

$$W_{\text{uptake}}\,(\%) = \frac{\text{mass}_{(\text{wet})} - \text{mass}_{(\text{dry})}}{\text{mass}_{(\text{dry})}} \times 100 \tag{1}$$

where $\text{mass}_{(\text{dry})}$ and $\text{mass}_{(\text{wet})}$ are the masses of the dry membrane and the membrane after the 24 h immersion respectively.

2.5. Pervaporation measurements

Pervaporation experiments were performed at 55 °C, according to the procedure described elsewhere [17], using 5 wt.% ethanol aqueous solutions under total pressure of 1 bar on the feed side and vacuum (10^{-2} m bar) on the permeate side. The effective membrane area was 12.5 cm^2. After achievement of the steady state, the permeate was collected for 1 h in cold traps immersed in liquid nitrogen. The compositions of feed and permeate were determined by gas chromatography using a Hewlett Packard 5890 chromatographer equipped with a SUPELCO WAXTM-10 capillary column (30 m × 0.53 mm × 1.0 μm film thickness) with oven temperature of 280 °C and flame ionization detector. Prior to the pervaporation experiments, the membranes were conditioned in the corresponding feed solutions overnight. The permeabilities (*P*) and selectivities were calculated according to procedure described in Ref. [14].

2.6. Membrane electrode assembly (MEA) preparation

Membrane electrode assemblies were prepared by hot pressing (80 °C) the membranes between two (anode and cathode) E-Tek electrodes for 2 min under pressure of 120 kg cm^{-2}. The electrodes composition is mentioned in the material part.

2.7. Direct ethanol fuel cell (DEFC) test

Membranes performances were evaluated in a commercial fuel cell test stand (Electrochem Inc. CompuCell GM gas management unit and Scribner Associates computer-controlled fuel cell test load Series 890B), shown in Fig. 1. The tubes for fluid circulation were made of steel with 6 mm internal diameter. The 5 wt.% ethanol feed aqueous solution was maintained in a closed steel recipient under stirring, before entering the anode part of the measuring cell at 1 bar. The liquid circulation (30 mL min^{-1}, 1 bar) was performed with a BVP-2 (Ismatec, Glattburg, Switzerland) gear pump. The cell (25 cm^2) was made of graphite with the design shown in Fig. 1 and has screws, which were closed at controlled torsion under 2 Nm. The temperature was controlled by a thermocouple directly inserted in the cell. The whole cell was kept in an oven with stabilized temperature. The cathode gas flow (synthetic air, 0.5 L min^{-1} at 2 bar) was controlled with a digital flowmeter. Air was saturated with water vapor. The operating temperatures were 25 °C, 60 °C and 90 °C. The uncertainty of the values recorded for the polarization curve was around 10%.

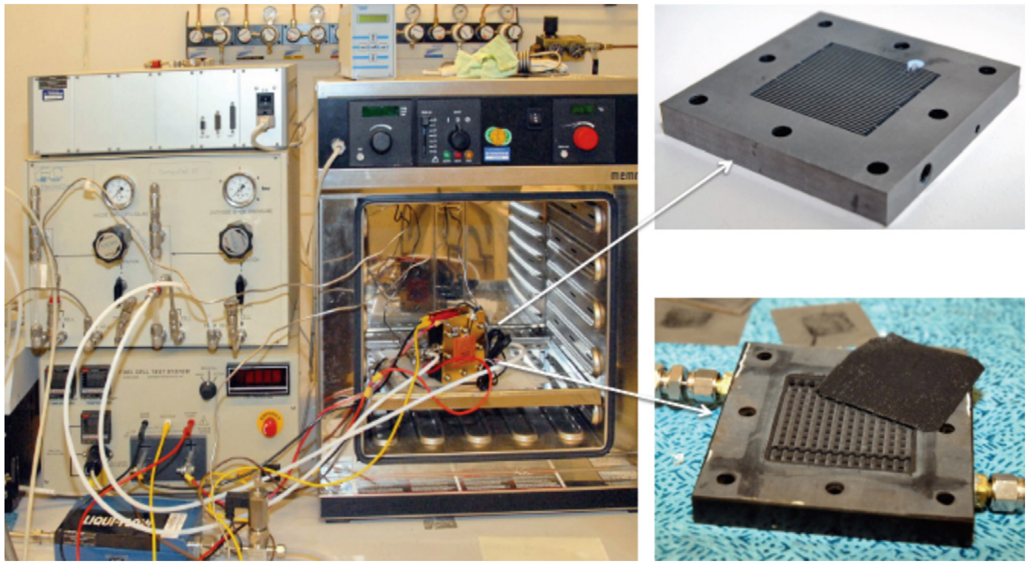

Fig. 1. DEFC test stand and measuring cells.

The ethanol crossover was estimated by measuring the CO_2 concentration at the cathode outlet, assuming that all CO_2 resulted from ethanol electro-oxidation at the cathode catalyst surface. The CO_2 sensor connected to the cathode outlet was a continuous non-dispersive infrared (NDIR) photometer (Advance Optima-High Performance Measurement Technology Infrared Analyzer Module Uras 14, ABB Automation Analytical Division) with gas filled opto-pneumatic detectors. The sensor works in the wavelength range 2–8 μm with a linearity deviation <1% of span.

3. Results and discussion

3.1. Membranes morphology (SEM Images)

Fig. 2 presents the SEM pictures of a 70/30 SPEEK/PI blend and a CMS-coated SPEEK membrane. From Fig. 2a and b it can be confirmed that preparation conditions for homogeneous blends could be reached. As reported before [15] for analogous membranes prepared for application in DMFC, the quality of films prepared at

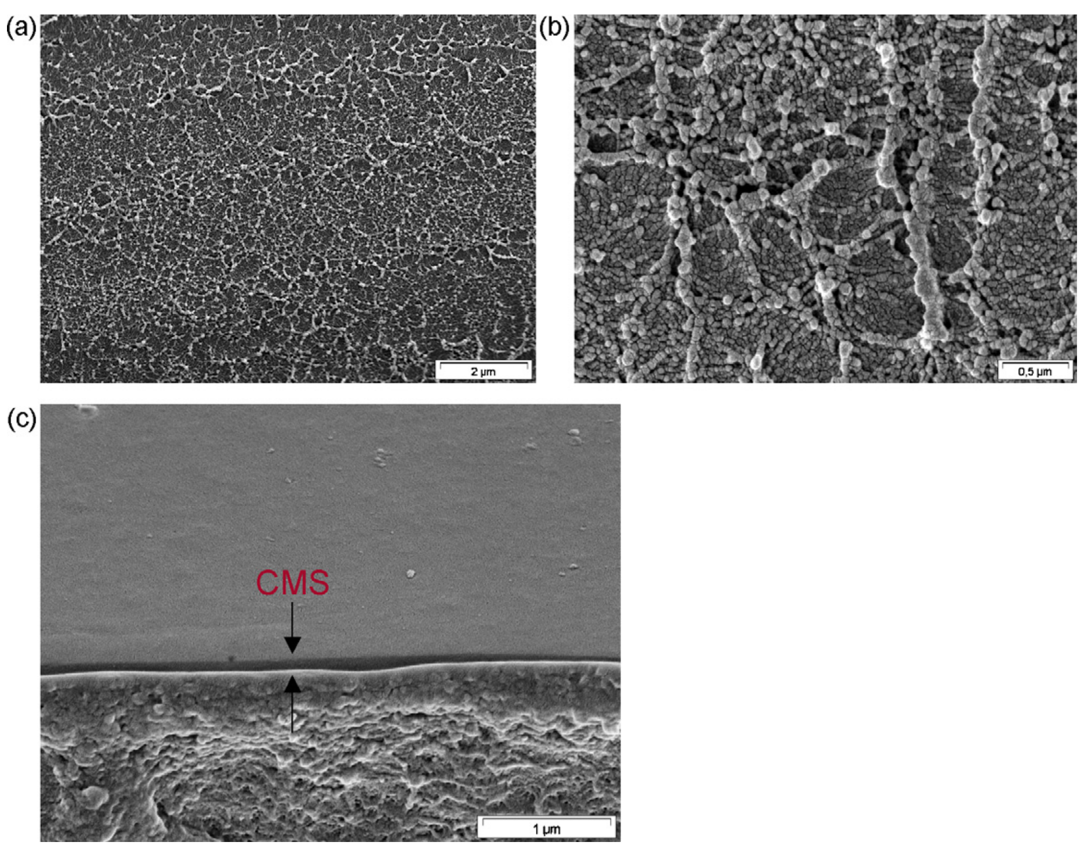

Fig. 2. SEM images of crossections of (a and b) 70/30 SPEEK/PI blend membranes and (c) CMS-coated SPEEK membranes.

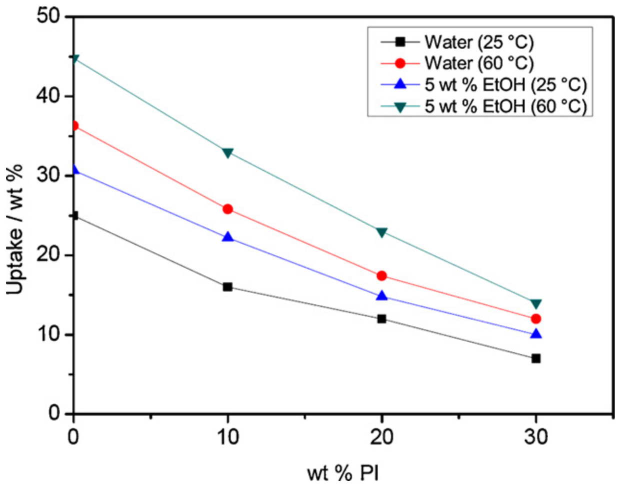

Fig. 3. Water and ethanol solution uptake results for Nafion 117®, plain SPEEK and 90/10, 80/20, 70/30 SPEEK/PI membranes.

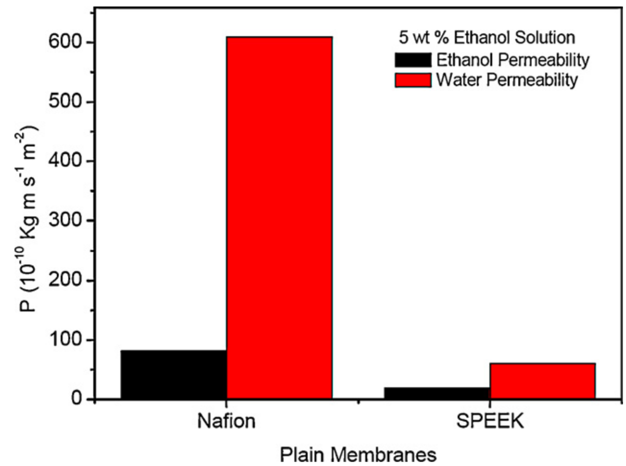

Fig. 4. Permeabilities of ethanol and water for Nafion 117® and plain SPEEK membranes at 60 °C.

different temperatures could be even visually checked. SPEEK/PI blends prepared with different wt.% of polyimide (10, 20 and 30) at 80 °C, 90 °C and 100 °C temperatures, respectively were opaque. But the SPEEK/PI blends prepared at higher temperatures (110 °C, 120 °C and 130 °C) were transparent and dense, indicating a complete mixing of the component polymers during the film formation. Fig. 2a shows the cross-section of one of the homogeneous SPEEK/PI blend prepared at high temperature. Other membranes prepared above 110 °C have a similar morphology.

Fig. 2c confirms that CMS-coated SPEEK membranes can be prepared with no crakes or any other kind of damage.

3.2. Water and ethanol solution uptake

Swelling of membranes in the alcohol solutions might directly affect the proton conductivity and mechanical properties of membranes. Fig. 3 represents the water uptake of membranes in de-ionised water and in 5 wt.% ethanol solution at 25 °C and 60 °C. It is evident that SPEEK water uptake capacity depends on temperature and PI-content in the blend. By incorporation of more hydrophobic polyimide into the blend, the water uptake capacity decreased from 25 to 7 wt.% at room temperature and from 36 to 12 wt.% at 60 °C for 70/30 SPEEK/PI blends. Analogous uptake decreases were also observed in experiments using ethanol solutions: from 32 to 10 wt.% and from 50 to 12 wt.% for the experiments at room temperature (25 °C) and at 60 °C respectively. Although the ethanol solution was very diluted, the presence of small amount of ethanol is enough to favour the uptake.

For the investigated CMS-coated SPEEK membranes the uptake with 5% of ethanol solution was around 42% for experiments at 60 °C and 28–30% for experiments at 25 °C. Water uptake is a bulk property. The CMS is a very thin layer (very low volume percent of the membrane) and therefore the water uptake is predominantly dependent only on the SPEEK layer. The thin CMS has practically no effect on water uptake, since water can reach and swell the SPEEK layer from the non-coated side, when the membrane is immersed in solution. There are no considerable changes in uptake value by adding the CMS layers.

The water and ethanol solution uptake of Nafion 117® is much higher than of all SPEEK membranes. The water uptake for Nafion 117® is ca. 28 wt.% at 25 °C and increases to 43 wt.% at 60 °C. With 5 wt.% ethanol aqueous solutions the uptake is 46 wt.% and 54 wt.% at 25 °C and 60 °C, respectively.

3.3. Pervaporation of alcohol and water

Water and ethanol permeabilities of the Nafion 117®, plain SPEEK, SPEEK/PI blends and CMS-coated SPEEK membranes were measured at 55 °C in pervaporation experiments. The thicknesses of all the membrane samples except Nafion 117® (200 um) were in the range of 65–75 μm. Fig. 4 shows that the permeabilities of ethanol and water for Nafion 117® are 5 to 6 times higher than plain SPEEK membrane.

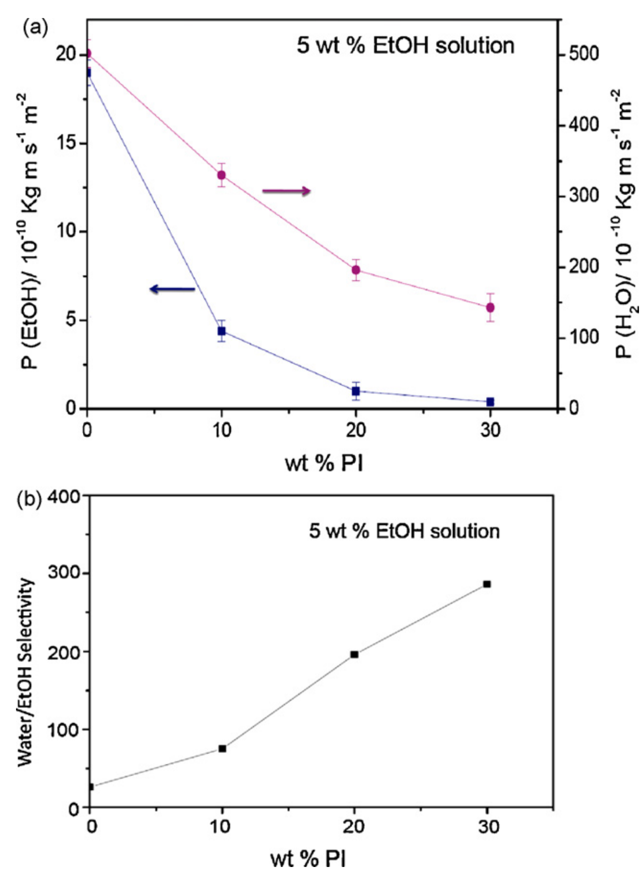

Fig. 5. Effect of polyimide contents on (a) the (■) ethanol and (●) water permeability and (b) water/ethanol selectivity of SPEEK/PI membranes. Feed solution: 5 wt.% ethanol aqueous solution.

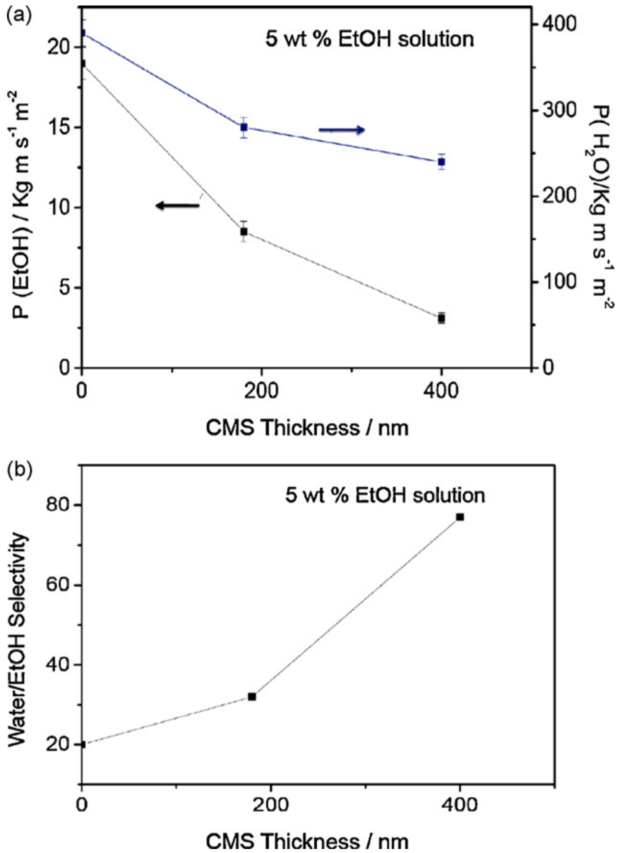

Fig. 6. (a) Effect of the CMS thickness on the (■) ethanol and (●) water permeability and (b) water/ethanol selectivity of bilayer membranes. Feed solution: 5 wt.% ethanol aqueous solution.

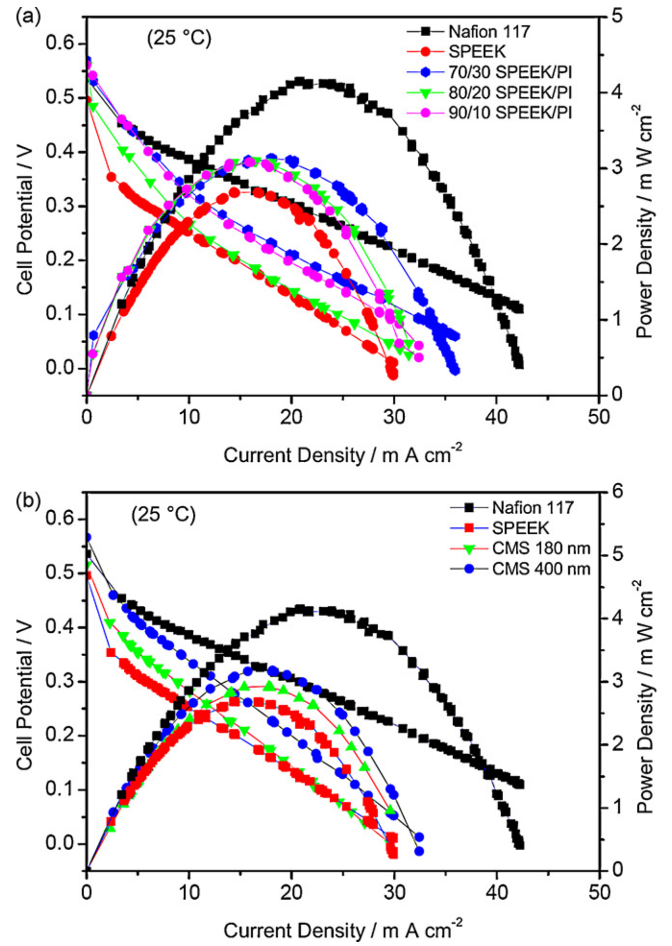

Fig. 7. Polarization and power density curves at operating temperature of 25 °C; (a) Nafion 117®, plain SPEEK and 90/10, 80/20, 70/30 SPEEK/PI blends and (b) Nafion 117®, plain SPEEK and CMS-coated SPEEK.

From Fig. 5(a) it is evident that the ethanol permeability was 50-fold smaller for 70/30 SPEEK/PI blend than for plain SPEEK and 150-fold smaller than for Nafion 117®. A gradual decrease of permeability is observed as the polyimide content in the blend increases since it is much less hydrophilic than SPEEK and Nafion 117®. The decrease of ethanol permeation is however much more evident than expected when considering just the dilution of sulfonic groups due to introduction of PI. The strong interaction between polymers reduces the swelling and therefore also the free space for water and ethanol transport. Fig. 5(b) shows that the water/ethanol selectivity increases up to 300 as the PI content in the blend membranes increases to 30 wt.%.

Fig. 6(a) shows the effect of the CMS layer on the rejection of ethanol molecules during pervaporation measurements. The permeabilities of ethanol was 6-fold and 20-fold decreased for the CMS (400 nm) coated SPEEK bilayer membranes when compared to plain SPEEK and Nafion 117® respectively.

As reported before [14] an advantage of CMS-coated membranes is that the CMS thin layer has practically no effect on the proton conductivity. However the water/ethanol selectivity is not as high as that of SPEEK/PI blend membranes. The maximum value obtained for the CMS (400 nm) coated SPEEK membrane was nearly 80, while for SPEEK/PI membranes the maximum selectivity value was near 300, as can be seen in Figs. 5b and 6b. The reason might be that the CMS pores are still larger than the ethanol molecule.

3.4. DEFC tests

The polarization curves (DEFC performance) for Nafion 117®, plain SPEEK, SPEEK/PI and CMS-coated SPEEK membranes were obtained at different temperatures (25 °C, 60 °C and 90 °C), but keeping other conditions like concentration of ethanol constant. The experiments were performed here with rather standard catalysts, which were not particularly optimized for DEFC. All the membranes were compared with the same catalyst and by attaching the electrode–catalyst layer to the membrane using the same procedure.

The results are compared in Figs. 7–9. Fig. 7(a) represents the polarization curves for the Nafion 117® and membranes of pure SPEEK and its three blends. The power and current densities obtained even with Nafion 117® are not high at room temperature and definitely the reason for that is the low catalytic activity. At this temperature the power and current densities for membranes based on the three SPEEK/PI blends are higher than for pure SPEEK but lower than for Nafion 117®. Nafion® has a higher proton conductivity than SPEEK or SPEEK/PI blends, the other membranes investigated here, according to measurements reported before [14,15] at the temperature range between 25 °C and 90 °C. At 25 °C the ethanol crossover in Nafion® membranes is not so high as at 60 °C and 90 °C. Therefore at this low temperature the effect of conductivity is predominant, when comparing Nafion® and SPEEK based membranes. However when plain SPEEK is compared with SPEEK/PI blends the proton conductivity is not the most important factor. SPEEK has higher proton conductivities than SPEEK/PI blends. However the blends have a better performance than the plain membrane at the same conditions. The reason is the low ethanol crossover through the blend membranes as compared to the pure SPEEK, which is confirmed in Fig. 10. There the molar frac-

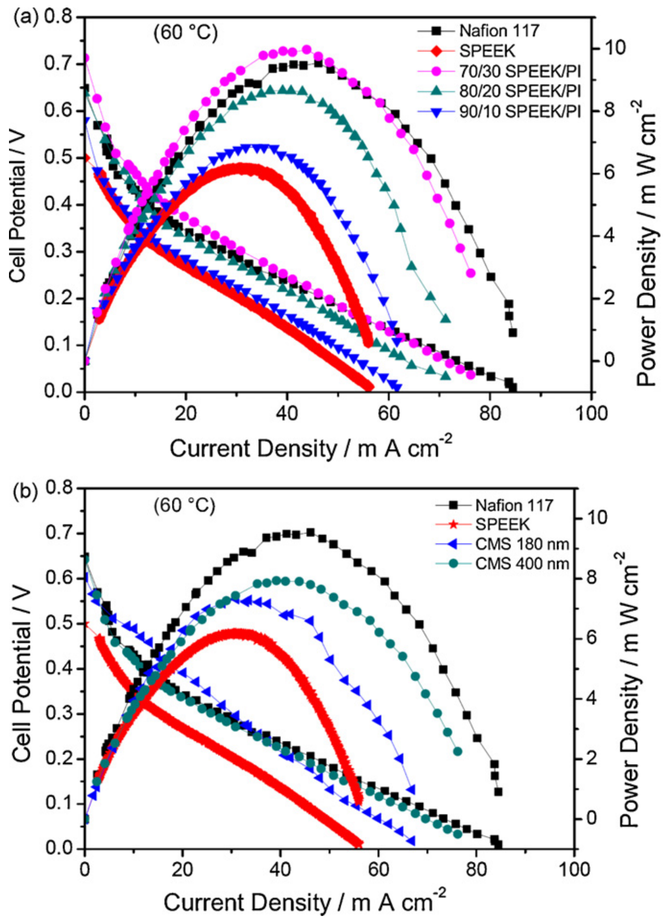

Fig. 8. Polarization and power density curves at operating temperature of 60 °C: (a) Nafion 117®, plain SPEEK and 90/10, 80/20, 70/30 SPEEK/PI blends and (b) Nafion 117®, plain SPEEK and CMS-coated SPEEK.

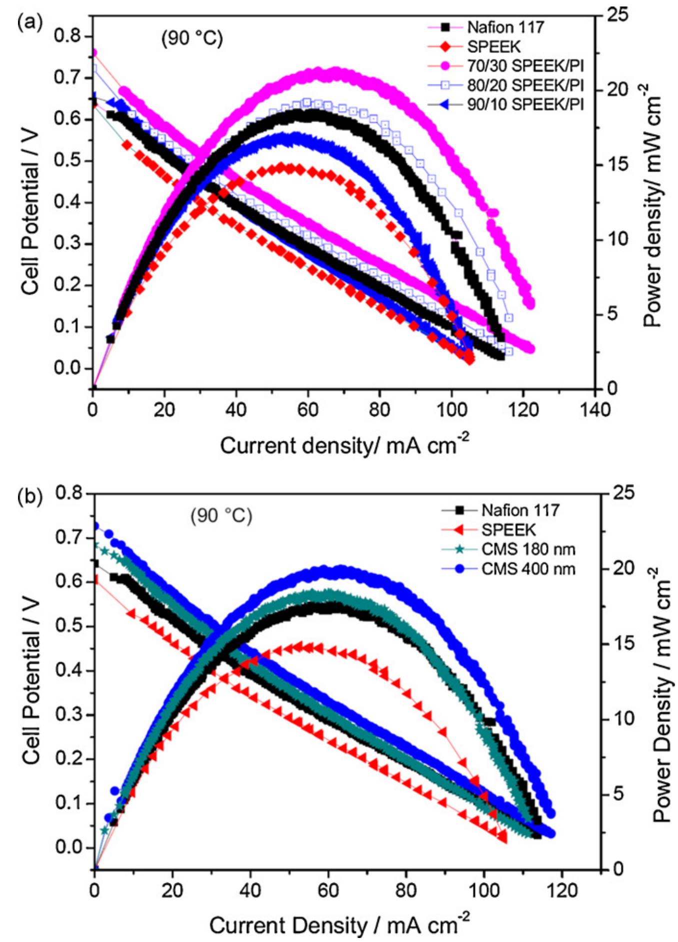

Fig. 9. Polarization and power density curves at operating temperature of 90 °C: (a) Nafion 117®, plain SPEEK and 90/10, 80/20, 70/30 SPEEK/PI blends and (b) Nafion 117®, plain SPEEK and CMS-coated SPEEK.

tion of CO_2 at the cathode outlet (ratio relative to the total of gases detected at the cathode), referred as "CO_2 crossover" is plotted versus PI concentration in the different blends. It is assumed that all the CO_2 is being formed in the cathode by the reaction of ethanol, which is crossing the membrane. The same situation is also observed during the DEFC performance tests at 25 °C for the CMS layer (180 nm and 400 nm) coated SPEEK membrane, yet the polarization and current densities curve are a bit higher than the pure SPEEK membrane but lower than Nafion 117®, as can be seen in Fig. 7(b). The effect of the CMS layer on the ethanol crossover through the membranes is shown in Fig. 11. For Nafion 117® the ethanol content at the cathode outlet is ca. 0.3%, which is not much higher than for the other membranes. When the DEFC tests were conducted at 60 °C (Fig. 8) the performances of all membranes were higher than those obtained at 25 °C, but an important difference can be observed in Fig. 8a. At high temperature the performances of all three SPEEK/PI blends are better than plain SPEEK and the blend with the highest PI content (70/30 SPEEK/PI) has a performance clearly superior than that of Nafion 117®. This is a result of the reduction of ethanol crossover due to the incorporation of polyimide in SPEEK matrix, leading automatically to the enhancement of the catalytic activities. By comparing the CO_2 content in the cathode outlet in experiments with different membranes under the same condition at 60 °C, the value for Nafion 117® membranes is 50% higher than the value for SPEEK, which is already much higher than for the blends, as shown in Fig. 10. By increasing the temperature, the swelling of Nafion® and SPEEK in the presence of ethanol aqueous solution increases considerably and the advantage of blending with a less swelling polymer is clear. At the same time the advantage of coating with a CMS layer becomes also significant. Fig. 8b shows the performance of CMS-coated SPEEK membranes at 60 °C in comparison to plain SPEEK and Nafion 117® membranes. From the polarization curves for the CMS-coated SPEEK membranes, the role of CMS nanoporous layer in the rejection of ethanol molecules during the DEFC

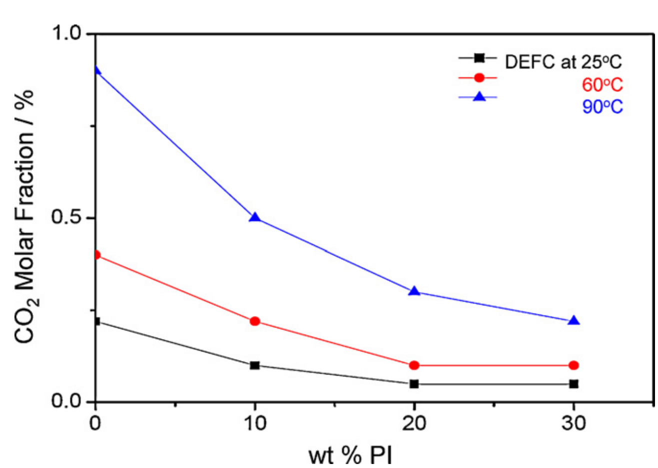

Fig. 10. CO_2 molar fraction at the cathode outlet ("CO_2 crossover") resulting from the ethanol reaction at the cathode, after crossing the membrane in DEFC experiments at different temperatures plotted as a function of the SPEEK/PI composition in the membrane.

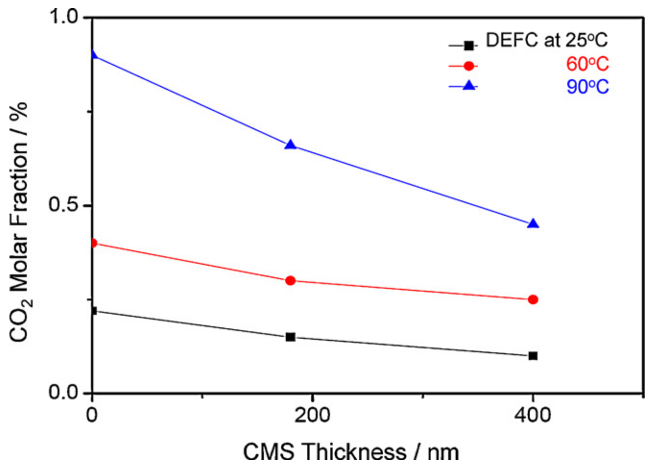

Fig. 11. CO_2 molar fraction at the cathode outlet ("CO_2 crossover"), resulting from the ethanol reaction at the cathode, after crossing the membrane in DEFC experiments at different temperatures, plotted as a function of the thickness of the CMS layer coating the SPEEK membrane.

performances is confirmed, leading to higher power and current densities as compared than the plain SPEEK membrane.

The ethanol crossover for SPEEK/PI blend membranes as well as for CMS-coated SPEEK membranes can be compared in Figs. 10 and 11 respectively. The measurements of CO_2 evolution in the cathode are a direct indication of the transport of ethanol through the membrane and conversion at the cathode. At 60 °C the rejection of ethanol by the SPEEK/PI blend membrane is higher than that of CMS-coated ones and this enhances the membrane performances and catalysts. Usually the DEFC tests reported in the literature are performed at higher temperature even above 100 °C, since the catalytic activity is much higher and the catalyst poisoning is lower at this condition [7 and 8]. The membranes prepared in this work were also tested at 90 °C using the same E-Tek electrodes. Fig. 9(a) shows the increase in the power densities and current densities for plain SPEEK and SPEEK/PI blend membranes compared to the DEFC performance at 60 °C. The two blend membranes with highest PI content (80/20 SPEEK/PI and 70/30 SPEEK/PI) have better performance than Nafion 117® at this high temperature. The performance of the Nafion 117® membrane did not increase with the increase of temperature from 60 to 90 °C and this can be understood, by taking in account the increase of ethanol crossover shown in Fig. 10 at 90 °C. The ethanol crossover for Nafion 117® was very high, particularly when compared to that of the SPEEK/PI blends. Also the uptake of ethanol aqueous solutions is much higher at 90 °C for Nafion 117®. The DEFC performance of the CMS-coated (180 nm) SPEEK membranes (Fig. 9b) at 90 °C is similar to that of Nafion 117®. The polariztion curves for Nafion 117® and both CMS-coated SPEEK membranes are similar, when considering 10% of experimental uncertainty. They are all clearly differentiated from the plain SPEEK membrane. By taking in account the power density, the membrane with thicker CMS layer is substantially better. Here the high power is also obtained because of low ethanol crossover through the bilayer membranes (Fig. 11). The CO_2 content at the cathode outlet at 90 °C for Nafion 117® is more than 8-fold higher than for the SPEEK/PI blends with highest PI content at the same temperature condition. However the ethanol crossover through the CMS-coated SPEEK membranes is still higher than through the SPEEK/PI blend membranes. Therefore for DEFC application the blend membranes seems to be much more interesting. Beside the performance advantage, they are easier to prepare in large scale.

4. Conclusion

Effective membranes for DEFC were prepared from two classes of materials. The first one is based on SPEEK coated with CMS layers and the second class is based on SPEEK/PI blends. Both approaches led a substantial reduction of ethanol crossover through the membranes, when compared to plain SPEEK and to Nafion 117® membranes. The reduction could be confirmed by permeability values obtained in pervaporation experiments and by measuring the CO_2 content in the cathode outlet in DEFC tests. The SPEEK/PI blends had better performance than CMS-coated SPEEK membranes in the DEFC tests. Particularly in DEFC experiments performed at 90 °C the SPEEK/PI membranes had a better than Nafion 117® membranes due mainly to the effective reduction of ethanol crossover.

Acknowledgments

The authors thank Karen M. Prause for the Scanning Electron Microscopy. The photographs in Fig. 1 were taken by Dr. S. Shishatskiy.

References

[1] S. Rousseau, C. Countanceau, C. Lamy, J.M. Leger, J. Power Sources 158 (2006) 18–24.
[2] C.B. Baretto, R.L.T. Parreira, R.R.D. Goncalves, C. Azevedo, J. Power Sources 185 (2008) 6–12.
[3] It's a global thing; Ethanol producer magazine August 2006.
[4] C. Xu, H. Wang, P.K. S. Shen, P. Jiang, Adv. Mater. 19 (2007) 4256–4259.
[5] E. Ribadeneira, B.A. Hoyos, J. Power Sources 180 (2008) 238–242.
[6] X. Xue, J. Ge, T. Tian, C. Liu, W. Xiang, T. Lu, J. Power Sources 172 (2007) 560–569.
[7] Q.G. Wang, Q. Sun, L. Cao, L.H. Jiang, G.X. Wang, S.L. Wang, S.H. Yang, Q. Xin, J. Power Sources 7 (2008) 142–147.
[8] F. Colmati, E. Antolini, E.R. Gonzalez, J. Power Sources 157 (2006) 98–103.
[9] E. Antolini, J. Power Sources 170 (2007) 1–12.
[10] A. Ghumman, C. Vink, O. Yepez, J. Power Sources 177 (2008) 71–76.
[11] T. Mathuraiveeran, K. Roelofs, T. Senftleben, Schiestel, Desalination 200 (2006) 662–663.
[12] A.R. Tan, L.M. Carvalho, F.G.R. Filho, A.S. Gomes, Macromol. Symp. 245–246 (2006) 470–475.
[13] G. Andreadis, P. Tsiakaras, Chem. Eng. Sci. 61 (2006) 7497–7580.
[14] H. Maab, S. Shishatskiy, S.P. Nunes, J. Membr. Sci. 326 (2009) 27–35.
[15] H. Maab, M. Schieda, W. Yave, S. Shishatskiy, S.P. Nunes, Fuel Cells 9 (2009) 401–409.
[16] S. Vetter, B. Ruffmann, I. Buder, S.P. Nunes, J. Membr. Sci. 260 (2005) 181–186.
[17] A. Dyck, D. Fritsch, S.P. Nunes, J. Appl. Polym. Sci. 86 (2002) 2820–2827.