Final Draft
of the original manuscript:

Maab, H.; Schieda, M.; Yave, W.; Shishatskiy, S., Pereira Nunes, S..:
SPEEK/Polyimide Blends for Proton Conductive
In: Fuel Cells (2009) Wiley

DOI: 10.1002/fuce.200800121

SPEEK/Polyimide blends for proton conductive membranes

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Abstract

A series of membranes based on sulfonated poly (ether ether ketone) (SPEEK)/ polyimide (PI) blends was prepared at different casting conditions. They were characterized by SEM, FTIR, DMTA, DSC, TGA, water /methanol pervaporation and impedance spectroscopy. The membranes prepared at 130oC from blends with 10, 20 and 30 wt % of PI are homogeneous, and the methanol permeabilities decreased from 28 x 10^{-10} Kg * m sec^{-1} m^{-2} (plain SPEEK) to 7.21, 2.61 and 0.55 x 10^{-10} Kg m sec^{-1} m^{-2} respectively. This corresponds to a 4 to 57-fold methanol cross-over reduction. With this improvement, by the introduction of PI the power density of SPEEK-based membranes in DMFC tests could be greatly improved.

1. Introduction

In a proton exchange membrane fuel cell (PEMFC), the proton conducting membrane (PEM) has the important function of transporting protons from anode to cathode, and at the same time it works as a barrier between cathodic and anodic reactant mixtures between the electrodes. In direct methanol fuel cells (DMFCs), the cell performance is reduced by the cross-over of fuel through the membrane towards the cathode [1- 6]. Nafion®, which is the most commonly used material as membrane in PEMFCs, presents both a significant methanol permeability in DMFCs [7], and loss of proton conductivity at high temperature when it is used in hydrogen/oxygen PEMFCs [8]. The sulfonated poly(ether ether ketone) (SPEEK) could be a promising membrane material for DMFC due to its thermal and mechanical stability and easy sulfonation of commercial poly (ether ether ketone) (PEEK). However although SPEEK has high proton conductivity at high sulfonation degree, it presents high methanol cross-over when is used in DMFCs.

Different attempts have been reported before to reduce the methanol cross-over. A review on these efforts has been published by Deluca and Elabd [9]. Blends of sulfonated poly (ether ether ketones) or poly (etherketone ketones) with different materials, including phenoxy resine, polyamide-imide (PAI), polyphenylsulfone, polyaniline, polyether sufone, polyether-imide (PEI), poly (vinylidene fluoride) and polyvinylpyrrolidone [8, 10- 19] aiming DMFC or other fuel cell related applications.. The approach followed by our group to reduce methanol crossover in polymeric membranes has been to develop different forms of nanocomposites using functionalized layered silicates, silica, polysilsesquioxanes, zirconium oxides and phosphates as fillers [20 - 23]. Recently a bilayer membrane was reported by our group for direct alcohol fuel cell, which was composed by a carbon molecular sieve layer obtained by the controlled pyrolysis of polyimide and an electrolyte layer of SPEEK [24]. In this paper, polyimide (PI) is directly blended to SPEEK to form a membrane with low methanol crossover. PI is much less hydrophilic than SPEEK, and at the same time a strong enough

interaction between both polymers allow the preparation of low swelling homogeneous membranes. Swier et al. [14] recently proposed the use of poly (ether ketone ketone) (SPEKK) blends with polyetherimide (PEI) as proton conductive membranes. In that case the blends were clearly heterogeneous blend with domains of about 0.5 μm. By choosing now another polyimide and the right casting conditions quite homogeneous blends are obtained with attractive properties for fuel cell.

2. Experimental:

2.1 Materials

The used polyimide for blend preparation was Matrimid® 5218, the polyimide resulted from the condensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and diamino-phenylindane) commercialized by Ciba Geigy (Switzerland). Before dissolution in dimethyl sulfoxide (DMSO), the polymer was dried in an oven at 120 °C for 24 h to remove any residual water. Poly (ether ether ketone) (PEEK), purchased from Victrex, was dried at 120°C under vacuum and sulfonated according to the procedure described elsewhere [25]. DMSO 99.9%, methanol 99.9% and ethanol 99.9% were purchased from Merck and used as received. For the fuel cell tests, electrodes and diffusion layers were purchased from E-Tek (BASF).

2.2 Preparation of SPEEK/PI blends

Blends of SPEEK (degree of sulfonation DS 56%) and polyimide (10, 20 and 30 wt. %) were prepared by dissolving both polymers in DMSO and casting as films from solution. Films with each composition were prepared at several different temperature ranges, from 80 °C to 130 °C with constant stirring for 24 hours. After the mixing step, SPEEK/PI films were prepared by casting the homogeneous polymer solution on clean glass plates which were heated at 100 °C for 24 hours, followed by an additional 24 hours 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.

2.3 Morphology

The morphology of the SPEEK/PI film cross-section was 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 it by Au/Pd sputtering.

2.4 FTIR Spectroscopy

FTIR spectra were obtained on a Bruker EQUINOX 55FTIR spectrometer equipped with attenuated total reflectance (ATR) accessory. All spectra were acquired at room temperature from 4000 to 550 cm^{-1} in N_2 atmosphere. The number of scans taken was 128 with spectral resolution of 2 cm^{-1}.

2.5 Water uptake

Water uptake was measured in de-ionised water and in 5 wt. % methanol solution at room temperature and at 60 ^{o}C. Before the water uptake experiments the pure SPEEK and blends were dried in a vacuum oven at 120 ^{o}C for 24 hours. 5.0 cm x 2.0 cm films were weighed and then immersed in de-ionised water and methanol solution for 24 hours. After that, and before weighting again, the excess water was quickly removed with tissue paper. The measurements were repeated three times, the results reported being the average values. The water uptake, W, of the blends was calculated according to the following equation

$$W(\%) = \frac{mass(wet) - mass(dry)}{mass(dry)} \text{x}100 \qquad (1)$$

Where mass $_{(wet)}$ and mass $_{(dry)}$ are the masses of the fully hydrated and the dry membrane respectively

2.6 Thermal properties

Dynamical mechanical thermal analysis (DMTA) was performed for SPEEK, PI and 70/30 SPEEK/PI blends cast at 130 ^{o}C and 80 ^{o}C to observe thermomechanical behaviour at different temperatures. Storage modulus (E'), loss modulus (E'') and loss tangent (tanδ) were measured in a RSA-II TA-instrument with a film tension mode at a frequency of 1 Hz. The test temperature was increased from 80 °C to 350 °C at a heating rate of 5 °C/min and a constant strain of 0.05 %.

Differential scanning calorimetry (DSC) of the blend membrane samples were characterized in the temperature range from 25 to 350 °C on a Netzsch DSC 204 calorimeter equipped with a refrigerated cooling system. Measurements, including baseline determinations were performed at the scan rate of 10K/min. The experiments were conducted in a nitrogen purge gas stream, and the glass transition (Tg) temperature values were obtained from the first scan thermograms.

Thermogravimetric analyses (TGA) were performed from 25 ^{o}C to 600 ^{o}C, in an argon stream with a Netzsch 209 instrument and a heating rate 10 K/min.

2.7 Pervaporation measurements

Pervaporation experiments were performed according to the procedure described elsewhere [26] using solutions of different concentrations at 55 ^{o}C, at a total pressure of 1 bar on the feed side, and vacuum (10^{-2} mbar) on the permeate side. The effective membrane area was 12.5 cm^2. After achievement of the steady state, the permeated was collected for 1 hour 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 (30m x 0.53 mm x 1.0 um film thickness) with oven temperature of 280^{o}C and flame ionization detector. Prior to the pervaporation experiments, the membranes were conditioned in the corresponding feed solutions overnight.

The permeabilities (P) were calculated according to equation (2):

$$P = \frac{m \cdot d}{A \cdot t} \qquad (2)$$

where: *m* is the mass of permeate; *d* is the thickness of membranes; *A* is the effective area of membrane in contact with the feed; *t* is the permeation time.

In membranes for pervaporation a commonly used parameter is the separation factor [27], which can be estimated according to equation 4:

$$\textit{Water/Alcohol Separation Factor} \;=\; \frac{C_F\,/(1-C_F)}{C_P\,/(1-C_P)} \qquad (3)$$

where C_F and C_P are the wt. % fractions of alcohol in the feed and permeate respectively.

In membranes for gases and vapours separation, the selectivity is defined by the ratio between the permeabilities of two permeant molecules [28], according to equation 4:

$$\textit{Water/Alcohol Selectivity} \;=\; P_{water}/\,P_{alcohol} \qquad (4)$$

In this paper the selectivity was calculated according to equation 4, which is more helpful in understanding the processes taking place in the fuel cell experiments.

2.8 Impedance measurement

The proton conductivities of plain SPEEK and SPEEK/PI blend membranes prepared with 10, 20 and 30 wt % polyimide were measured by impedance spectroscopy by using a Zahner IM6 Electrochemical workstation. Impedance spectra were scanned in a frequency range from 10^6 to 10 Hz, at dc bias potential of 0V and with signal amplitude of 5 mV. Before the measurement the membranes were conditioned in de-ionised water for 24 hours at room temperature. Five pieces of membranes (with total thickness around 500 μm) were stacked in between the two diffusion layers (carbon cloth) in a through-plane conductivity cell.

Measurements were carried out at 100% relatively humidity and at temperature varying from 40°C to 100°C.

2.9 Membrane Electrode Assembly (MEA) preparation

Membrane electrode assemblies (MEA) were prepared with the SPEEK/PI membranes prepared by hot pressing of the membranes between two E-Tek electrodes. The E-Tek cathode electrode was loaded with 100% pure platinum black catalyst (4 mg/cm^2), while the E-Tek anode electrode was loaded with an alloy of 60% Pt Ru (3mg/cm^2) on Vulcan XC-72.

2.10 Fuel cell test

Membrane performances were evaluated in a commercial DMFC test stand (Electrochem Inc. CompuCell GM gas management unit, and Scribner Associates computer-controlled fuel cell test load Series 890B). The DMFC experiments were performed as described before [3]. The cell (25cm^2) was fed with a solution of methanol (5 wt.%) in water (30mL/min, 1 bar) on the anode side and synthetic air (0.5L/min at 2 to 3 bar) on the cathode side. The operating temperature was 60°C.

3. Results and Discussion

3.1 Membrane preparation and morphology

Fig 1 presents some of the SEM pictures of the SPEEK/PI blends prepared at different temperatures. The quality of the films was first visually checked after drying. Blends prepared with different wt. % of polyimide (10, 20 and 30) at 80 ^{o}C, 90 ^{o}C and 100 ^{o}C were turbid . The SEM images of these blends (Fig. 1b, d and f) confirm that they are heterogeneous. On the other hand, the blends prepared at higher temperatures (110 ^{o}C, 120 ^{o}C and 130 ^{o}C) were transparent and the SEM images (Fig. 1a, c and e) have only a very fine structure in the nanometer scale, confirming the homogeneity. Swier et al. [14] investigated a similar system

(SPEKK/PEI). In that case a heterogeneous morphology was observed with large separated domains. A finer phase-separated morphology was observed at higher temperatures but still with domains in the size of 0.5 μm. The obtainment of a finer structure was attributed to the faster evaporation of solvent. Mikhailenko et al. [18] investigated membranes prepared from SPEEK and PEI. They observed phase segregation with domain size around 1 μm and 2-3 μm in blends respectively containing 5 and 25 % PEI. The morphology of SPEEK/PI blends prepared in this work is highly dependent on the casting temperature. A practically homogeneous membrane even at high magnification could be obtained when cast at temperatures higher than 110^{o}C. The blend homogeneity is discussed further below taking in account the glass transition temperatures.

For understanding the phase behavior and the resulting morphology, the phase diagram of binary SPEEK/PI blends was theoretically estimated. The phase diagram can be obtained experimentally or by using the Flory-Huggins theory based on the Gibbs energy of mixing [29 – 30]. Here, the phase diagram was estimated by using the Flory-Huggins theory, and the calculation of the binodal curve for the SPEEK/PI blend, was carried out by the mathematical procedure and considerations proposed by Horst and Wolf [30, 31]. A rough estimation of the solubility parameter was done by the group contribution method [32]. For this calculation the SPEEK was considered having one sulfonic group per monomer unit (100 % sulfonation degree).

Fig. 2 shows the theoretical phase diagram, as well as the experimental data, mentioning if the blend was transparent or turbid at that preparation condition. The characteristic UCST phase separation behavior could be confirmed. The critical temperature (T_c) was estimated as ~260 °C which is far from the casting temperature (80-130 °C). The reasons for the overestimated T_c can be the following: a) the polymer molecular weights (M_w) were assumed to be very high to allow mathematical approximations during the calculation. However the real M_w values for SPEEK and PI used in this work were 171 Kg/mol and 72 Kg/mol respectively. For these

values, the approximation is not completely valid anymore. It is expected that lower molecular weight entropically favors polymer mixing and would enlarge the one-phase region of the phase diagram, contributing to a T_c shift to lower temperatures; b) The used calculation model was quite simple and the values of Flory-Huggins interaction parameter were roughly estimated without taking in account specific strong interactions between the acid sulfonic groups in SPEEK and the imide groups in PI. The formation of electron donor-acceptor complexes have been reported before [33], for similar blends like SPEEK/poly (amide imide). Preferential strong interaction could considerably increase the homogeneous phase region in the diagram; c) A third important assumption for the rough estimation of the phase diagram is that the system is practically binary, neglecting the influence of the solvent. In reality the membrane formation starts from a ternary system containing solvent. During the evaporation the composition changes and the binary blend is obtained. A homogeneous solution could be formed in all cases even at temperatures lower than the casting condition. The solvent acts therefore as compatibilizer for SPEEK and PI. Even small amounts of solvent might shift the phase separation curve to lower temperatures.

A last important factor is again related to the presence of solvent and takes in account not only the thermodynamic of the phase separation predicted by the phase diagram but the kinetics of phase separation and membrane formation as well. As mentioned above, during the membrane formation the composition of the solution layer, which will give rise to the final membrane, is changing constantly with the solvent evaporation. Even if a two phase system would be thermodynamically expected for the binary blend at the casting temperature, demixing might not occur when the last part of the solvent leaves the film if the mobility of the polymer chains at the final stage of solvent evaporation is low enough,. A homogeneous morphology would be frozen leading to a transparent membrane. This frozen state is maintained at room temperature and at the operation temperature.

The following films were chosen for further characterization: SPEEK, PI and 70/30 SPEEK/PI blends prepared by solution casting at 130 ^{o}C (homogeneuous membrane) and 80 ^{o}C (heterogeneous membrane).

3.2 FTIR study

ATR-FTIR spectra for polyimide, SPEEK and 70/30 SPEEK/PI (130 ^{o}C) blend were obtained and can be seen in Fig 3. The blend contains all the peaks of polyimide and SPEEK. As expected, peaks characteristic of polyimides are diluted in the blend with SPEEK. Peaks that can only be assigned to polyimide in the blend include the methyl group C-H stretching (2957–2863 cm^{-1}), C=O (symmetric stretching) (1779 cm^{-1}), C=O (anti-symetric stretching) (1721 cm^{-1}), CNC (axial stretching) (1371 cm^{-1}) and CNC (out of plane bending) (719 cm^{-1}). The peaks corresponding to SPEEK sulfonic group (O=S=O) symmetric and asymmetric vibrations are (1009 cm^{-1}), (1076 cm^{-1}) and (1217 cm^{-1}). In the blend, the first two of these peaks are shifted to lower frequencies (1079 cm^{-1}) and (1219 cm^{-1}) due to the hydrogen bonding between the hydrogen attached to the sulfonic group of SPEEK and the nitrogen or oxygen atoms of polyimide [34]. This is an evidence of a strong interaction between polymers, thus the assumption of bimodal curve shifted at lower temperatures is possible, and therefore it leads to produce homogeneous blends.

3.3 Water Uptake

Proton conductivity and mechanical properties of membranes are directly affected by water absorption (membrane swelling). Fig 4 represents the water and water/methanol solution absorption for SPEEK, and 90/10, 80/20 and 70/30 SPEEK/PI blends cast at 130 ^{o}C. The blend samples were immersed in de-ionized water and 5 wt% methanol solution at room temperature and then at 60 ^{o}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 prominently, form 24 to 10 wt % at room temperature and from 35 to 11 wt % at 60 ^{o}C for the 70/30 SPEEK/PI. In the same way the water uptake capacity also decreased from 40 to 12 wt % and from 51 to 14 wt % for methanol solution at room and at 60 ^{o}C respectively. The water absorption of 70/30 SPEEK/PI (130 ^{o}C) blend is lower than that of Nafion 117 [35].

3.4 Thermal properties

Fig 5 shows the DMTA thermograms of pure polyimide, SPEEK and of two blends obtained with the same composition but different mixing temperatures (70/30 SPEEK/PI cast at 80 ^{o}C and 130 ^{o}C). The glass transition temperature (Tg) of the polyimide was around 318 ^{o}C. Two Tg values (240 ^{o}C and 295 ^{o}C) were recorded for the 70/30 SPEEK/PI blend cast at 80 ^{o}C, confirming that the component polymers are not miscible at 80 ^{o}C. The Tg related to the SPEEK chains in the 70/30 SPEEK/PI blend cast at 130 ^{o}C is shifted from 224 (for pure SPEEK) to 255 ^{o}C, indicating at least a partial miscibility due to strong interaction between SPEEK and PI. The presence of an eventual additional higher Tg could not be confirmed for the blend cast at 130^{o}C, since the sample was mechanically not stable above 290^{o}C to allow the DMTA analysis in this temperature range. For this reason DSC experiments were performed.

The Tg for SPEEK, PI and the 70/30 SPEEK/PI blends cast at 80 ^{o}C and 130 ^{o}C can be estimated from the DSC runs shown in Fig 6. Tg values for SPEEK and PI obtained by DSC are 210 ^{o}C and 305 ^{o}C respectively. Above 280^{o}C SPEEK starts to loose the sulfonic groups as detected by thermalgravimetric analysis (discussed later). This degradation might be responsible for the apparent additional transitions above this temperature seen in the SPEEK curve. For the 70/30 SPEEK/PI cast at 80 ^{o}C 4 transitions can be clearly seen: 210, 305^{o}C, which practically coincides with the Tg of the componente polymers and two much less evident additional transitions around 245 and 280^{o}C. An explanation for these additional

transitions could be that at the interface between phases of practically pure polymers there is enough interaction between small parts of the chains to shift their Tg. By DTMA the Tgs corresponding to isolated SPEEK and PI could be clearly seen as peaks. The additional transitions appeared as shoulders. For membranes cast at 130°C only one transition can be observed around 250°C by DSC. This confirms the homogeneity of the membrane and the miscibility of SPEEK and PI at 130°C, at least as far as domains as small as 15 nm are concerned. DSC and DTMA usually are able to detect 2 Tgs in a blend only if different phase domains are larger than this limit [36]. The measured Tg for the SPEEK/PI blend by DSC is not far from the value obtained by DTMA, and that stimated by using the Fox equation:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \qquad (5)$$

where T_g, T_{g1} and T_{g2} are the glass transition temperatures of the blend, polymer 1 and 2; w_1 and w_2 are the weight fractions of polymer 1 and 2, it is possible to estimate that for a miscible blend with 70 wt % SPEEK and 30 wt % PI the expected Tg would be around 235 °C. However this is just a first approximation. For blends with strongly interacting polymers other equations have been proposed in the literature and reviewed by Utracki [37]. However this is not the focus of this paper. By DTMA a small shoulder below 250°C could also be observed, what might indicate the presence of a small amount of another phase richer in SPEEK, but highly dispersed in the predominant SPEEK/PI matrix. DTMA is known to be more sensitive than DSC to differentiate coexistent phases with similar T_g's [38].

To evaluate the thermal stability of the blend, TGA analyses were performed and the results are shown in Fig 7. For polyimide most of the mass loss occurs near 500 °C and for the SPEEK membranes two mass loss curves can be observed; one near 300 °C which is usually assigned to the loss of sulfonic groups and the other at around 500 °C which shows the degradation of the backbone. The thermogravimetric curves for the 70/30 SPEEK/PI blends

cast at 80°C and especially for those cast at 130 °C are not as prominent around 300 °C as that for pure SPEEK , due to the presence of polyimide.

3.5 Pervaporation of alcohol and water

Water and methanol permeability through the pure SPEEK and three blend membranes (90/10 SPEEK/PI, 80 /20 SPEEK/PI and 70/30 SPEEK/PI prepared at 130 °C) were measured at 55 °C by pervaporation and they are shown in Fig. 8 (a) . The thicknesses of the membrane samples were 70 ± 5 μm. By addition of PI in the SPEEK, the methanol permeability decrease is possible without sacrificing the proton conductivity. Thus, the 70/30 SPEEK/PI (130 °C) blend has the lowest values of methanol and water permeability: 0.55 x 10^{-10} Kg * m s^{-1} m^{-2} and 100 x 10^{-10} Kg*m s^{-1} m^{-2} respectivelly. In both cases a gradual decrease of permeability is observed as the polyimide content in the blend increases since it is much less hydrophilic than SPEEK. The decrease of methanol 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 methanol transport.

3.6 Proton conductivity

The proton conductivities for plain SPEEK and three blend samples at 100% RH were plotted as a function of the temperature in Fig 9. The results show a decrease in proton conductivity as an effect of polyimide addition to the SPEEK matrix. For blends with 30 wt.% of PI, the proton conductivity decrease is only around 25% compared to plain SPEEK. While the proton conductivity in blends are lower than SPEEK and Nafion®, the methanol permeability decrease provides membrane with enhanced fuel cell performance. Table 1 shows the "relative selectivity" of pure SPEEK, and three of its blends with polyimide, based on their proton conductivity and methanol permeability performed at 60 °C. The relative selectivity

defined as the ratio of proton conductivity to the methanol permeability is sometimes used as an indication of the potential performance in DMFC tests. The value for Nafion® and for some other blends reported in the literature [6, 8, 23] are included for comparison. A gradual increasing tendency is observed for the SPEEK/PI blends with increase of polyimide content. The 80/20 SPEEK/PI (130 °C) and 70/30 SPEEK/PI (130 °C) blends have much higher (more than 40-fold) relative selectivity than Nafion®.

3.7 DMFC tests

The polarization curves (DMFC performance) for plain SPEEK and its blends (90/10, 80/20 and 70/30 SPEEK/PI-membranes cast at 130 °C) were obtained and compared in Figure 10. It is quite evident from the polarization and power density curves that the difference in performance between the membranes was significant, the blends being superior. This is a result of the reduction of methanol crossover due to the incorporation of polyimide in SPEEK matrix. In accordance to the pervaporation and relative selectivity values, the optimal membranes are those blends prepared with 20 and 30 wt. % of PI and cast at 130 °C. They have higher power density and current density than pure SPEEK membranes.

4. Conclusions

A series of SPEEK/PI blend membranes was prepared by casting from solution at different temperatures. Structural and thermal characterization of the blend membranes prepared at 110 °C, 120 °C and 130 °C confirmed their homogeneity. Compared to pure SPEEK membrane, the membranes prepared from blends cast at 130^{o}C have methanol permeability 4 to 57-fold lower and better performance in DMFC tests.

Acknowledgment

The authors thank Karen M. Prause for the scanning electron microscopy and H. Böttcher for the thermal mechanical measurement.

References

[1] A. Heinzel, V. M. Barragán; A review of the state-of-the-art of the methanol crossover in direct methanol fuel cells. *J. Power Sources* 84 (1999) 70–74.

[2] J. Cruickshank , K. Scott; The degree and effect of methanol crossover in the direct methanol fuel cell. *J. Power Sources* 70 (1998) 40–47.

[3] K. Scott; W. M. Taama, P. Argyropoulos, K. Sundmacher; The impact of mass transport and methanol crossover on the direct methanol fuel cell. *J. Power Sources* 83 (1999) 204–216

[4] V. S. Silva, B. Ruffmann, H. Silva, V. B. Silva, A. Mendes, L. M. Madeira, S. Nunes; Zirconium oxide hybrid membranes for direct methanol fuel cells - Evaluation of transport properties. *J. Membrane Sci.* 284 (2006) 137–144.

[5] V. Antonucci, A. S. Arico, V. Baglio, J. Brunea, I. Buder, N. Cabello, M. Hogarth, R. Martin, S. Nunes; Membranes for portable direct alcohol fuel cells. *Desalination* 200 (2006) 653–655.

[6] H. Cai, K. Shao, S. Zhong, C. Zhao, G. Zhang, X. Li, H. Na; Properties of composite membranes based on sulfonated poly(ether ether ketone) (SPEEK)/phenoxy resin (PHR) for direct methanol fule cell usages. *J. Membrane Sci.* 297 (2007) 162–173

[7] M. V. Williams, H. R. Kunz, J. M Fenton. Operation of Nafion(TM)-based PEM fuel cells with no external humidification: influence of operating conditions and gas diffusion layers". *J. Power Sources* 135 (2004) 122–134.

[8] C. Zhao, Z.Wang, D. Bi, H. Lin, K. Shao, T. Fu, S. Zhong H. Na; Blend membranes based on disulfonated poly(aryl ether ether ketone) (SPEEK) and poly(amid imide) (PAI) for direct methanol fuel cell usages. *Polymer* 48 (2007) 3090–3097.

[9] N. W. Deluca and Y. A. Elabd, Polymer Electrolyte Membranes for the Direct Methanol Fuel Cell: A Review. *J. Polymer Sci.: Part B: Polymer Phys.* 44 (2006) 2201-2225.

[10] J. A. Kerres. Development of ionomer membranes for fuel cells, *J. Membrane Sci.* 185 (2001) 3-27.

[11] H.-Y. Jung and J.-K. Park, Blend membranes based on sulfonated poly (ether ether ketone) and poly (vinylidene fluoride) for high performance direct methanol fuel cell. *Electrochimica Acta* 52 (2007) 7464-7468.

[12] H. L. Wu, C. C. M. Ma, F. Y. Liu, C.-Y. Chen, S.-J. Lee, C.-L. Chiang, Preparation and characterization of poly (ether sulfone) / sulfonated poly (ether ether ketone) blend membranes. *European Polymer J.* 42 (2006) 1688-1695.

[13] J. Roeder, V. Zucolotto, S. Shishatskiy, J. R. Bertolino, S. P. Nunes, A. T. N. Pires; Mixed conductive membranes: Aniline polymerization in an acid SPEEK matrix. *J. Membrane Sci.* 279 (2006) 70–75

[14] S. Swier, M.T. Shaw, R.A. Swei; Morphology of sulfonated poly(ether ketone ketone) poly(ether imide) blends and their use in proton exchange membranes, J.Membr.Sci. 270 (2006) 22 – 31

[15] J.V. Gasa, R.A. Weiss, M.T. Shaw; Structured polymers electrolyte blends based on sulfonated polyetherketoneketone (SPEKK) and polyether imide (PEI); J.Membr.Sci.320 (2008) 215 – 223.

[16] M. L. Di Vona, A. D. Epifanio, D. Marani, M. Trombetta, E. Traversa, S. Licccia, SPEEK/PPSU-based organic-inorganic membranes: proton conducting electrolyte in anhydrous and wet environments. *J. Membrane Sci.* 279 (2006) 186–191

[17] F. G. Wilhelm, I. G. M. Punt, N. F. A. Vander Vegt, H. Strathmann, M. Wessling. Cation permeable membranes from blends of sulfonated poly(ether ether ketone) and poly(ether sulfone). *J. Membrane Sci.* 199 (2002) 167–176.

[18] S. D. Mikhailenko, S. M. J. Zaidi, S. Kaliaguine; Electrical properties of sulfonated poly(ether ether ketone)/poly(etherimide) blend membranes doped with inorganic acids. *J. Polymer.Sci. Part B: Polym. Phys.* 38 (2000) 1386–1395.

[19] H. L. Wu, C. C. M. Ma, H. C. Kuan, C. H. Wang, C. Y. Chen, C. L. Chiang; Sulfonated poly(ether ether ketone)/poly(vinylpyrrolidone) acid-base polymer blends for direct methanol fuel cell application. *J. Polymer.Sci. Part B: Polym. Phys.* 44 (2006) 565–572.

[20] S. P. Nunes, B. Ruffmann, E. Rikowski, S. Vetter, K. Richau; Inorganic modification of proton conductive polymer membranes for direct methanol fuel cells. *J. Membrane Sci.* 203 (2002) 215–225.

[21] C. S. Karthikeyan, S.P. Nunes, L. A. S. A. Prado, M. L. Ponce, H. Silva, B. Ruffmann and K. Schulte; Polymer nanocomposite membranes for DMFC application. *J. Membrane Sci.,* 254 (2005) 139–146

[22] V. S. Silva, B. Ruffmann, S. Vetter , A. Mendes, L. M. Madeira, S. P. Nunes; Characterization and application of composite membranes in DMFC, *Catalysis Today* 104, (2005) 205–212

[23] R. Gosalawit, S. Chirachanchai, S. Shishatskiy, S. P. Nunes, Sulfonated montmorillonite/ sulfonated poly (ether ether ketone) (SMMT/SPEEK) nanocomposite membrane for direct methanol fuel cells (DMFCs). *J. Membrane Sci.* 323 (2008) 337-346.

[24] H: Maab, S. Shishatskiy, S. P. Nunes, Preparation, characterization of bilayer carbon/polymer membranes. *J. Membrane Sci.* (2008).

[25] D. Gomes, I. Buder, S. P. Nunes, Sulfonated silica-based electrolyte nanocomposite membranes. *J. Polymer Sci. Part B: Polymer Physics,* 44 (2006) 2278-2298.

[26] A. Dyck, D. Fritsch, S. P. Nunes; Proton conductive membranes of sulfonated poly phenylsulfone, *J. Appl. Polymer Sci.* 86 (2002) 2820–2827.

[27] H. E. A. Brüschke; State-of-art of pervaporation processes in the chemical industry (Part II, Chapter 3). In S. P. Nunes and K. V. Peinemann, editors, "Membrane Technology in the Chemical Industry", Wiley-VCH, Weinheim, Germany, 2001, 2nd edition, 2006.

[28] S. P. Nunes and K. V. Peinemann; Membrane Materials and Membrane Preparations (Part I). In S. P. Nunes and K. V. Peinemann, editors, "Membrane Technology in the Chemical Industry", Wiley-VCH, Weinheim, Germany, 2001, 2nd edition, 2006.

[29] E.M. Woo, K.Y. Cheng, Y. Chen, C.C Su, Experimental verification on UCST phase diagrams and miscibility in binary blends of isotactic,syndiotactic and atactic polypropylenes, Polymer 48 (2008) 5753 – 5766.

[30] R.Horst, calculation of the phase diagrams not requiring the derivatives of the Gibb energy demonstrated for a mixture of two homopolymers with corresponding copolymers, Macromol theory simul, 4 449 – 458 (1995).

[31] R. Horst , B.A Wolf, Calculation of critical points not requiring the derivatives of the Gibb,s energy demonstrated for mixture of two homopolymers with the corresponding copolymers, Macromol theory simul 5, 81 – 92 (1996).

[32] P. A. Small, Some factors affecting the solubility of polymers. *J. Appl. Chem.* 3 (1953) 71-79.

[33] R. J. Karcha and R. S. Porter, Miscible blends of modified poly (aryl ether ketone) with aromatic polyimides, J. Polymer Sci. B: Polym. Phys. 31, 821 (1993)

[34] P. Krishnan, J. Park, C. Kim; Preparation of proton conducting sulfonated poly(ether ether ketone)/boron phosphate composite membranes by in situ sol-gel process. *J. Membrane Sci.* 279 (2006) 220–229.

[35] H. Wu, C. M. Ma, C. Li, T. Lee, C. Chen, C. Chiang, C. Wu, Sulfonated poly(ether ether ketone)/poly(amid imide) polymer blends for proton conducting membranes. *J. Membrane Sci* 280 (2006) 501–508.

[36] T. G. Fox, Influence of diluent and of copolymer on the glass temperature of a polymer system. *Bull. Am. Phys. Soc*. [2] 1 (1956) 123.

[37] L. A. Utracki, *Polymer Alloys and Blends, Thermodynamics and Rheology*, Hanser Publishers, Munich, Vienna, New York, 1989.

[38] D. Pinoit, R. E. Prud'homme, DSC and DTMA characterization of ternary blends, *Polymer* 43 (2002) 2321-2328.

Figure Captions

Figure 1. SEM images of SPEEK/PI blend membranes cast at different temperatures: (a, c, e) at 130 °C and (b, d, f) at 80 °C; membranes with different PI content: (a. b) 10 wt. %,. (c, d) 20 wt. %, and (e, f) 30 wt. %.

Figure 2. (■) Theoretical phase diagram; Experimental observations: (○) transparent and (●) turbid films after solvent evaporation.

Figure 3. FTIR spectrum of polyimide, SPEEK and a 70/PI SPEEK/PI film cast at 130^{o}C.

Figure 4. Water uptake of 70/30 SPEEK/PI films cast at 130 °C.

Figure 5. DMTA analysis (Tan δ vs. Temperature/^{o}C) of PI, SPEEK and 70/30 SPEEK/PI cast at 80 and 130^{o}C.

Figure 6. DSC thermograms of PI, SPEEK and 70/30 SPEEK/PI cast at 80 and 130^{o}C.

Figure 7. TGA curves of PI, SPEEK and 70/30 SPEEK/PI cast at 80 and 130^{o}C.

Figure 8. Effect of polyimide contents (membrane cast at 130^{o}C) on the methanol and water.permeability measured at 55^{o}C. Feed solution: 5 wt. % methanol aqueous solution.

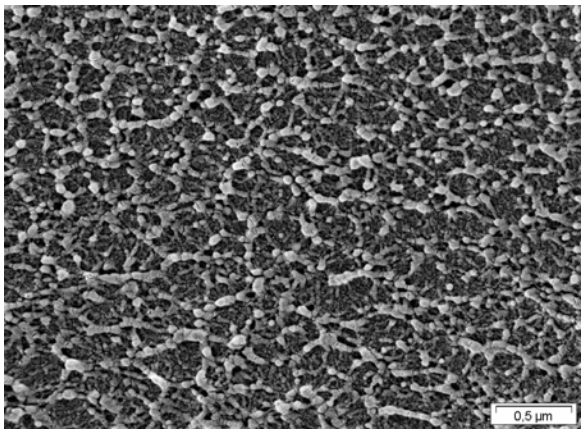
Figure 9. Proton conductivity as a function of temperature for PI, SPEEK and blends measured at 100 % relative humidity.

Figure 10. Polarization and power density curves for plain SPEEK and SPEEK/PI membranes.

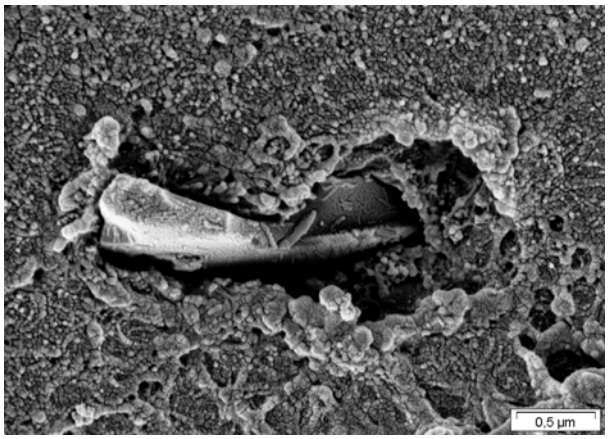
Table 1. Proton conductivity, methanol permeability and relative solubility for the membranes prepared in this paper compared to other membranes from the literature.

Membrane	T / ^{o}C	Conductivity[a] / 10^{-3} S cm^{-1}	Methanol permeability / 10^{-8} cm^{2} s^{-1}	Relative selectivity / 10^{4} S s cm^{-3}	Ref.
SPEEK (DS 56 %)	60	36	3.4 [b]	106	This paper
SPEEK (DS 55 %)	60	40	3.0 [c]	133	23
90/10 SPEEK/PI	60	33	0.9 [b]	367	This paper
80/20 SPEEK/PI	60	28	0.3 [b]	933	This paper
70/30 SPEEK/PI	60	25	0.06 [b]	4167	This paper
Methyl SPEEK (IEC 1.92 meq/g)	80	134	147 [c]	9	6
75/25 Methyl SPEEK (IEC 1.92 meq/g) / phenoxy resin	80	79	54 [c]	15	6
SPEEK copolymer (IEC 2.50 meq/g	80	167	261 [c]	6	8
80/20 SPEEK (IEC 2.50 meq/g)/PAI	80	98	85 [c]	11	8
Nafion 117	60	85	9.5 [c]	89	23

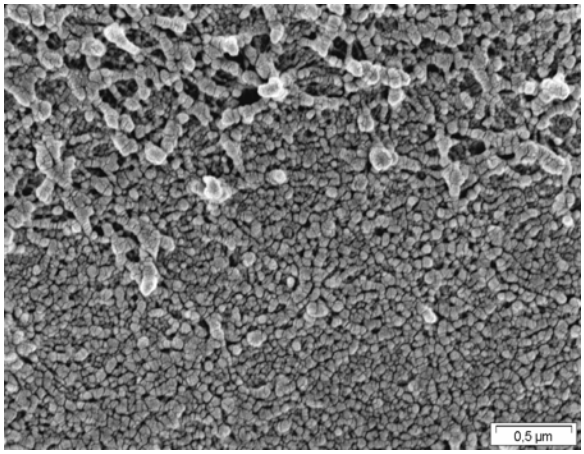
[a] measured by impedance spectroscopy at the indicated temperature
[b] measured by pervaporation at 55^{o}C
[c] diffusion coefficients measured at the indicated temperature



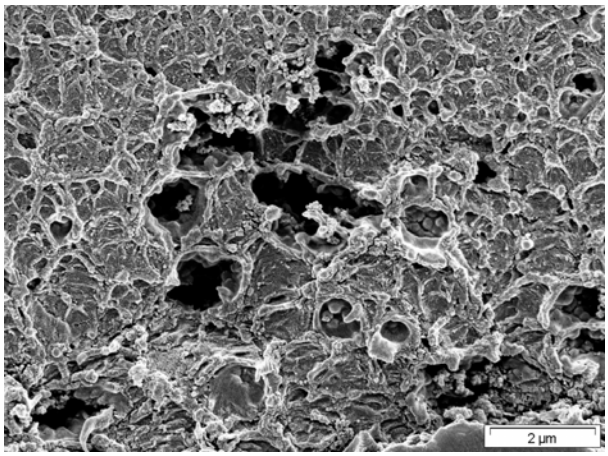
a)



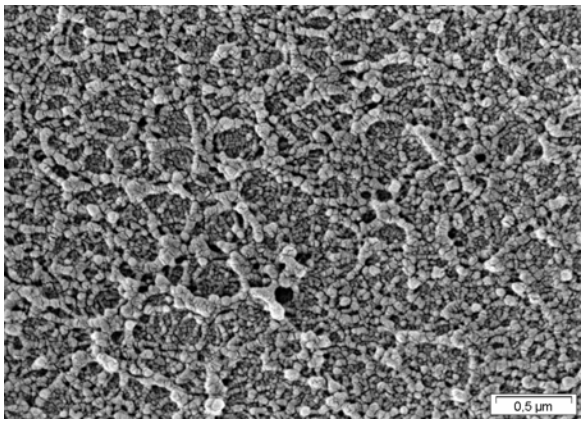
b)



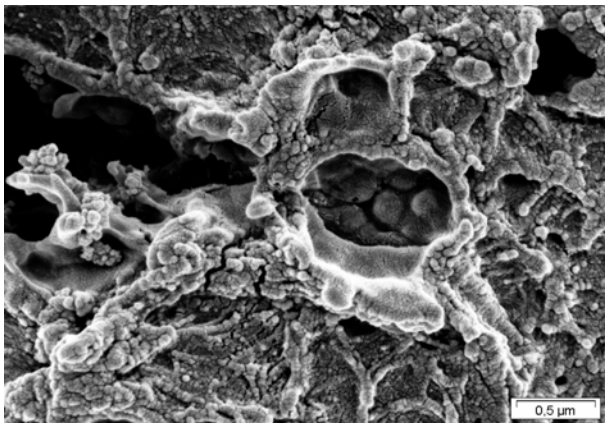
c)



d)



e)



f)

Figure 1

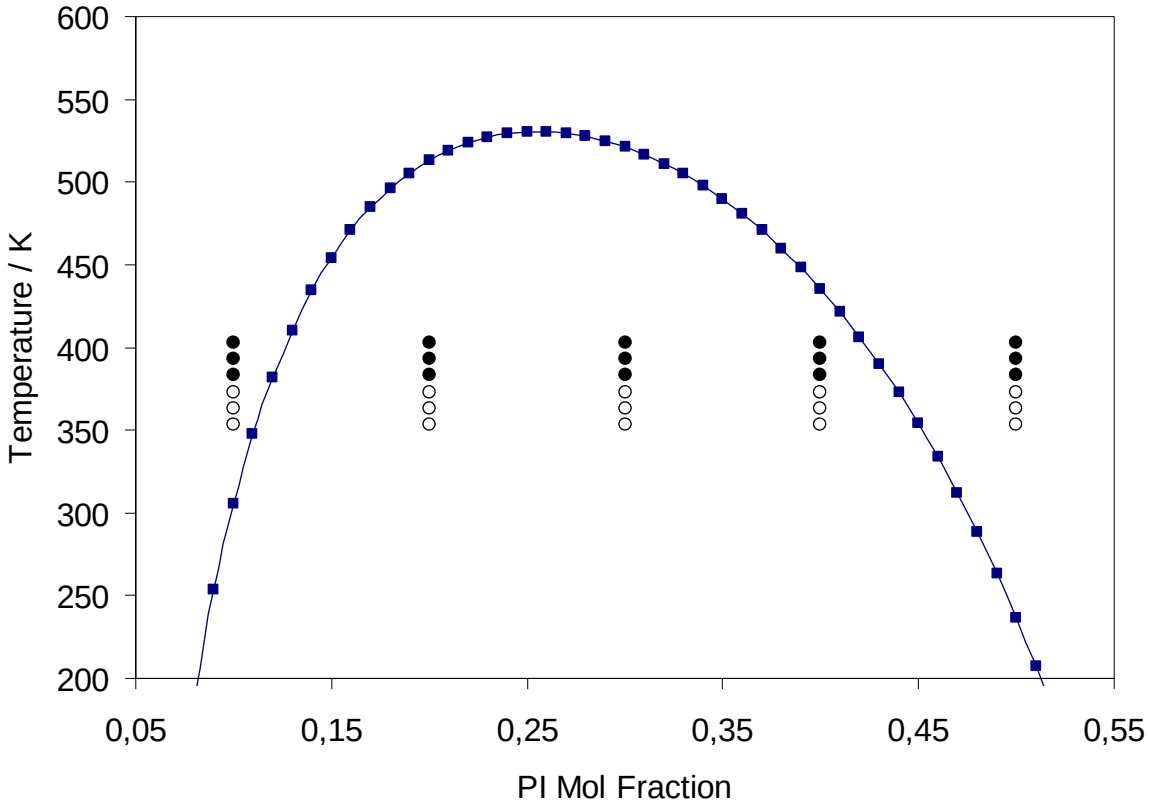

600
550
500
450
400
350
300
250
200
Temperature / K
0,05
0,15
0,25
0,35
0,45
0,55
PI Mol Fraction

Figure 2

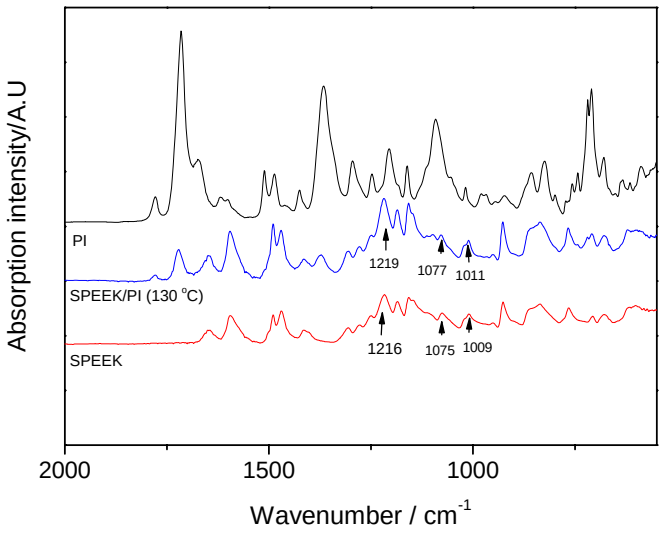

Absorption intensity/A.U
PI
1219
1077
1011
SPEEK/PI (130 °C)
1216
1075
1009
SPEEK
2000
1500
1000
Wavenumber / cm-1

Figure 3

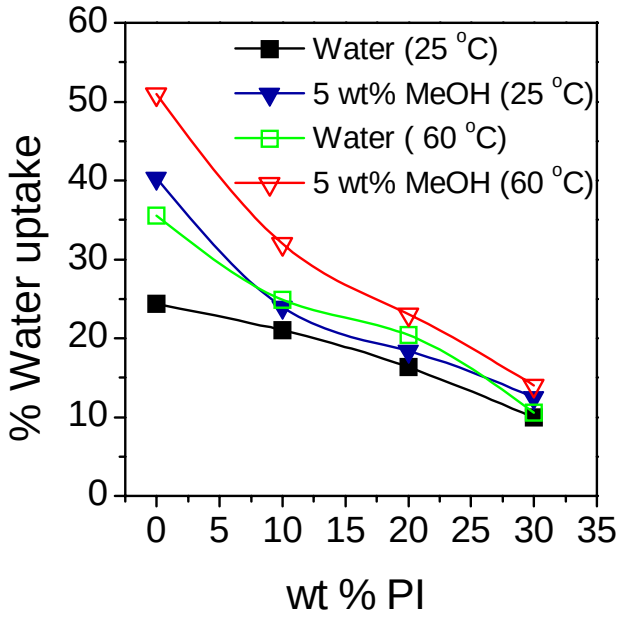

Water (25 °C)
5 wt% MeOH (25 °C)
Water (60 °C)
5 wt% MeOH (60 °C)
% Water uptake
wt % PI
0
10
20
30
40
50
60
0
5
10
15
20
25
30
35

Figure 4

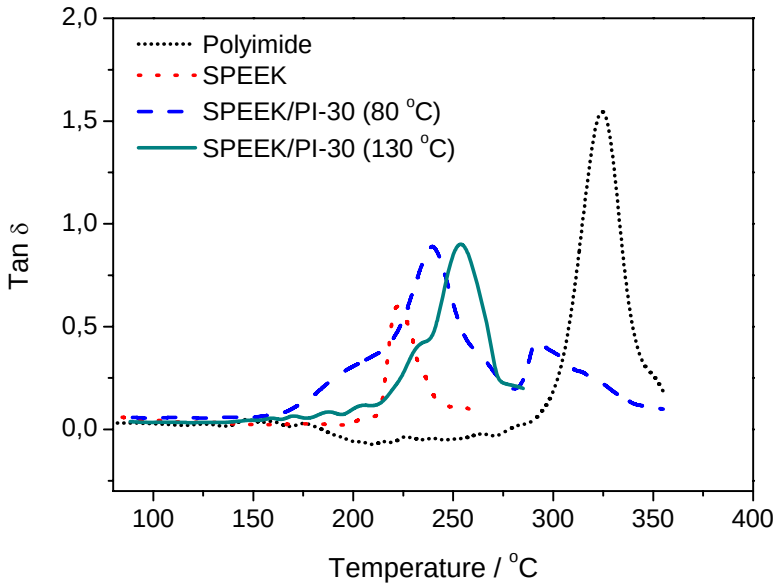

2,0
1,5
1,0
0,5
0,0
Tan δ
Polyimide
SPEEK
SPEEK/PI-30 (80 °C)
SPEEK/PI-30 (130 °C)
100
150
200
250
300
350
400
Temperature / °C

Figure 5

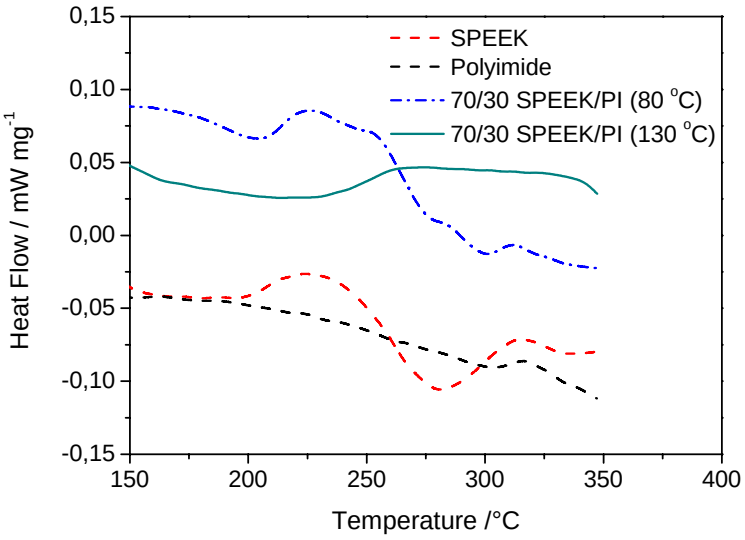

SPEEK
Polyimide
70/30 SPEEK/PI (80 °C)
70/30 SPEEK/PI (130 °C)
Heat Flow / mW mg-1
0,15
0,10
0,05
0,00
-0,05
-0,10
-0,15
150
200
250
300
350
400
Temperature /°C

Figure 6

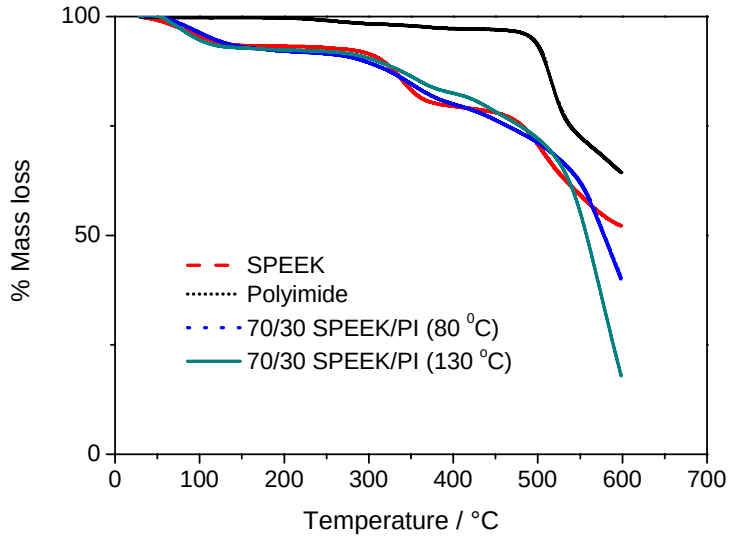

100
50
0
% Mass loss
0
100
200
300
400
500
600
700
Temperature / °C
SPEEK
Polyimide
70/30 SPEEK/PI (80 °C)
70/30 SPEEK/PI (130 °C)

Figure 7

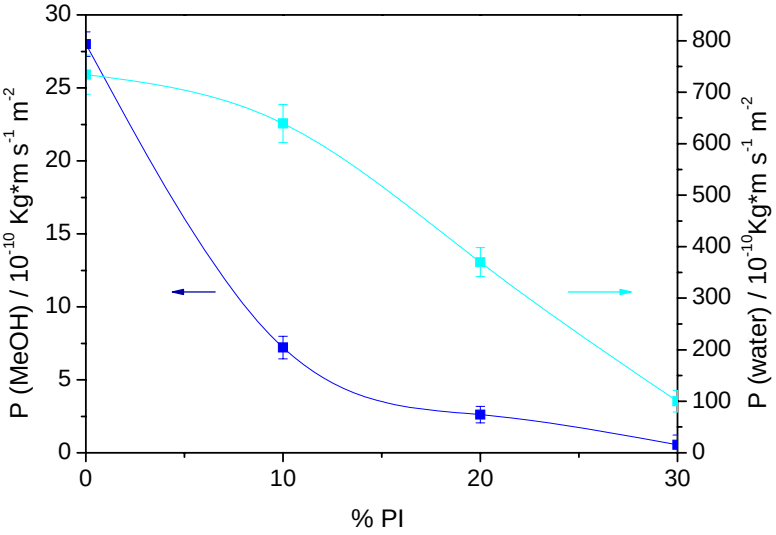

P (MeOH) / 10^-10 Kg*m s^-1 m^-2
P (water) / 10^-10 Kg*m s^-1 m^-2
% PI
0
5
10
15
20
25
30
0
100
200
300
400
500
600
700
800
0
10
20
30

Figure 8

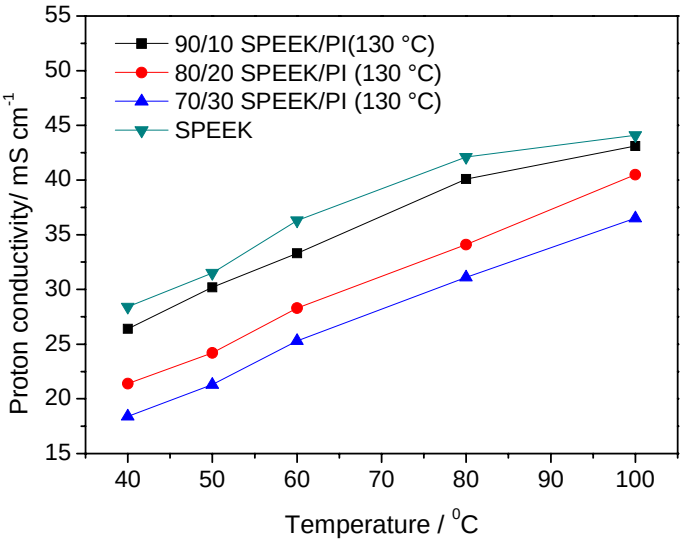

90/10 SPEEK/PI(130 °C)
80/20 SPEEK/PI (130 °C)
70/30 SPEEK/PI (130 °C)
SPEEK
Proton conductivity/ mS cm-1
Temperature / 0C
55
50
45
40
35
30
25
20
15
40
50
60
70
80
90
100

Figure 9

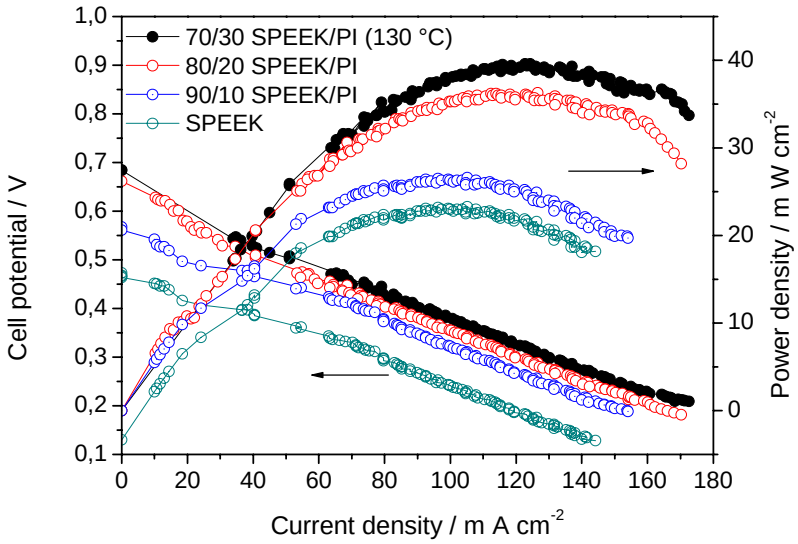

70/30 SPEEK/PI (130 °C)
80/20 SPEEK/PI
90/10 SPEEK/PI
SPEEK
Cell potential / V
Power density / m W cm-2
Current density / m A cm-2
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
20
40
60
80
100
120
140
160
180
40
30
20
10
0

Figure 10