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NEW POLYMER ELECTROLYTE MEMBRANE BASED ON SULFONATED POLYSULFONE BLENDS

Blends of an aromatic copolymer bearing polar pyridine units in the main chain with sulfonated polysulfone (SPSF) were prepared in order to improve the copolymer's acid uptake and conductivity values. Depending on blend composition and sulfonation level miscible pairs were obtained as was studied by dynamic mechanical analysis. Blends of SPSF with sulfonation degree 70% and increased composition of the copolymer were selected for further study. The thermal and oxidative stability, the doping ability and the proton conductivity of the blends were also tested. Finally, an initial single cell test was performed with one of the prepared blends, showing promising results.

Key words: membrane, copolymer, polysulfone, stability, fuel cells.

Fuel cells are alternative energy sources which consist of an anode, cathode and an electrolyte and convert the chemical energy of a fuel (H₂) directly into electrical energy and heat. Among the different types of fuel cells, PEMFCs have attracted much attention for use in automobile applications due to their high efficiency and the possibility of zero-emission during operation. Hydrogen is attractive as a fuel because its oxidation product (water) is environmentally benign, lightweight and highly abundant [1]. Although fuel cells have been operated efficiently for more than 40 years [2], they have not yet been widely used in vehicular transportation, electric utility and other applications [1], largely because of their cost. To make this technology commercially competitive, better anode, cathode and electrolyte materials are needed.

An increase of the operation temperature [3] of PEMFCs has many advantages. At high temperatures the CO tolerance of the electrodes is enhanced enabling thus the use of hydrogen produced by reforming of natural gas, methanol or gasoline. At the same time, high temperature operation improves water and thermal management and increases the rates of reaction, diffusion and proton conductivity. Consequently, all the system simplifies and the efficiency is increased. For these reasons, it is desirable to move hydrogen PEMFCs technology towards a high temperature (150–200°C) operation.

Up to now the perfluorinated polymers electrolytes such as Nafion (DuPont) [4], Flemion (Asahi Glass), Dow Membrane (Dow Chemical), GoreSelect (W.L. Gore and Associates) and Aciplex (Asahi Chemical) have been used for PEMFCs applications. However, their high cost and low performance at temperatures higher than 100°C hinder their application in the high temperature PEMFCs. Therefore, there is a demand for new polymer

membranes [5–12] combining the properties of perfluorinated membranes with the requirements for high temperature operation.

Great efforts are made to develop proton conducting membranes for operation at high temperatures. The ideal polymer membrane electrolyte [13] in such a fuel cell should exhibit chemical and electrochemical stability under operating conditions, mechanical strength and stability and compatibility to the other components of the cell. Furthermore, it is necessary to have low permeability to the reactants (H₂, O₂) and high charge transport. Finally, the electrolyte should exhibit high proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity and last production cost has to be compatible with the intended application.

It is known that polysulfone exhibits excellent mechanical, thermal and chemical stability. Sulfonation of polysulfone has generated great interest because of the increase of the glass transition temperature and the good properties [14,15]. Besides increasing hydrophilicity with the introduction of ionic groups into polysulfone, these sulfonated polysulfones have been used as ion-exchange membranes. Increase of the sulfonation degree increases water or acid uptake but at the same time reduces the mechanical stability of the polymer. Blends of the sulfonated polymers [16,17] with other polymers, which can result in miscible systems, because of acid-base interactions, seem to overcome this problem.

In the present study polymeric electrolytes composed of blends with acid-base interaction were prepared. Blends of an aromatic copolymer bearing polar pyridine units in the main chain [18,19] with sulfonated polysulfone were studied in the attempt to combine the mechanical integrity of the copolymer and the high proton conductivity, after doping with phosphoric acid, of the sulfonated polysulfone. Blends with sulfonation degree 70% and increased composition of the copolymer were selected for further study.

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EXPERIMENTAL

Materials

2,5-Bis(4-hydroxyphenyl)pyridine and PPy(50)coPSF were prepared according to literature [18,19]. Bisphenol A, Bis(4-fluorophenyl)-sulfone and polysulfone were obtained from Aldrich. Sulfonated polysulfone was prepared according to literature procedures [20]. The sulfonation degree (percentage of the introduced sulfonate group to polysulfone) of SPSF was determined by ^1H NMR spectroscopy. Solvents were obtained from Aldrich or Merck. The polymeric structures used are presented in Scheme 1.

Instrumentation

Dynamic mechanical analysis measurements were carried out using a Solid-state Analyzer RSA II, Rheometrics Scientific Ltd. at 10 Hz. Thermogravimetric analysis was carried out by a DuPont 990 thermal analyzer coupled to a DuPont 951 TGA accessory. Conductivity measurements were carried out by the four-probe current interruption method using a potentiostat/galvanostat (EG and G model 273) and an oscillator (Hitachi model V-650F).

Membrane Preparation

PPy(50)coPSF was dissolved in dimethylacetamide at room temperature. SPSF was also dissolved in the same solvent at room temperature. PPy(50)coPSF/SPSF blends were obtained by mixing of the two solutions, each time at the proper ratio. All mixtures were cast on glass plates and the solvent slowly evaporated at 70°C . The resulting membranes were dried under vacuum at 120°C for 3 days to remove any excess of solvent.

Doping behavior

The membranes were immersed into 85% H_3PO_4 solution at various temperatures and doping times in order to obtain the maximum doping level. The wet membranes were wiped dry and quickly weighed again. The acid uptake of membranes is reported in weight percent as follows:

$$\text{acid uptake} = (W_{\text{wet}} - W_{\text{dry}}) \times 100 / W_{\text{dry}}$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

Fenton's test

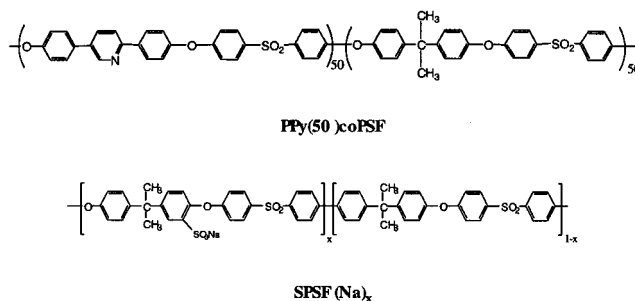
Membrane samples were immersed into 3% H_2O_2 aqueous solution containing 4 ppm $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at 80°C for 72h [21,22]. The weights of dried samples before and after the experiment were compared. The oxidative stability of the samples was examined with dynamic mechanical analysis and thermogravimetric analysis.

MEA preparation of PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend

The membrane was doped as previously described, at a doping level of 100%wt. Its thickness after doping was $140 \mu\text{m}$. The electrodes were prepared using carbon cloth purchased by E-TEK and Pt/C 2.8–6.0%. The loading of the electrodes was 0.5 mg/cm^2 while PBI was used as ionomer. The weight ratio of Pt/PBI was 1/1. The membrane electrode assembly was constructed by hot pressing of the two electrodes and the polymer membrane at 150°C for 10 min under a pressure of 100 kg/cm^2 . The MEA performance was finally studied in a home made single cell $2 \times 2 \text{ cm}^2$.

RESULTS AND DISCUSSION

Our approach for the development of new high temperature polymer membranes is based on the blending of two polymers having complementary properties. In the case of polymer blends, miscibility is expected in cases where polymers bear proper groups which can participate in specific interactions. The studied here polymer pair can form acid-base interactions due to the presence of the pyridine rings in the copolymer PPy(50)coPSF and the sulfonate groups of SPSF(Na) (Scheme 1). In this way the excellent mechanical properties of the PPy(50)coPSF is expected to be combined with the higher doping ability of the SPSF especially with high sulfonation degree.



Scheme 1. Copolymer PPy(50)coPSF/SPSF(Na)

Blends of PPy(50)coPSF/SPSF(Na)_x with various degrees of sulfonation and compositions are reported in Table 1 for copolymer's molecular weight 160.000.

Table 1. Composition of PPy(50)coPSF /SPSF(Na)_x blends

Blends	Composition
PPy(50)coPSF/SPSF(Na) ₄₅	75/25
PPy(50)coPSF/SPSF(Na) ₇₀	75/25
PPy(50)coPSF/SPSF(Na) ₉₀	75/25
PPy(50)coPSF/SPSF(Na) ₇₀	70/30
PPy(50)coPSF/SPSF(Na) ₇₀	60/40
PPy(50)coPSF/SPSF(Na) ₇₀	50/50
PPy(50)coPSF/SPSF(Na) ₇₀	25/75

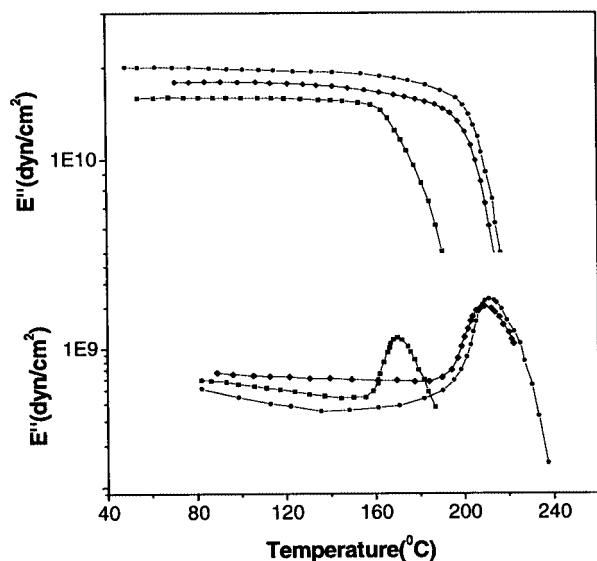


Figure 1. Temperature dependence of the storage (E') and loss modulus (E'') of PPy(50)coPSF/SPSF(Na)_x 75/25 blends for different sulfonation degrees $x=45$ (—■—), $x=70$ (—●—), $x=90$ (—◆—)

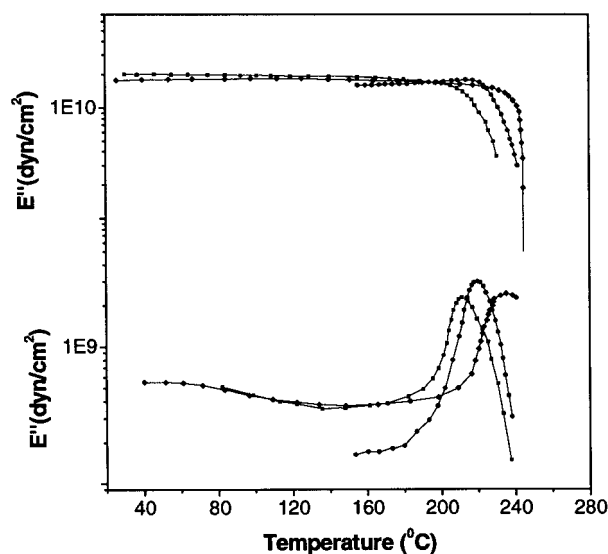


Figure 2. Temperature dependence of the storage (E') and loss modulus (E'') of PPy(50)coPSF/SPSF(Na)₇₀ blends: 75/25 (—■—), 70/30 (—●—), 60/40 (—◆—)

First of all, blends of the same composition but different sulfonation degrees were prepared in order to see the influence of the sulfonation degree in the miscibility. The certain composition was 75/25 (Table 1). As shown in Figure 1 the glass transition temperature of the blend is increased as the sulfonation degree is increased.

The SPSF(Na)₇₀ was further selected in order to prepare blends at various compositions (Table 1). Blend composition rich in PPy(50)coPSF showed good film forming properties and gave films with mechanical integrity while PPy(50)coPSF/SPSF(Na)₇₀ 50/50 and 25/75 blends were brittle. The dynamic mechanical analysis of the copolymer rich blend compositions is shown in Figure 2. Due to the observed miscibility the glass transition temperature is increased as the SPSF(Na)₇₀ content is increased. All blends show glass transition temperature above 200°C and thermal and oxidative stability.

The membranes retained their mechanical integrity and their thermal stability after treatment with hydrogen peroxide denoting their high oxidative stability. As an example, the PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend is reported here whose thermal and oxidative stability was studied with thermogravimetric analysis before and after treatment with H₂O₂ as shown in Figure 3.

Furthermore, the doping behavior of some of the prepared membranes was studied. Firstly, blends of the same composition but different sulfonation degree of SPSF(Na)_x were selected in order to see the influence of the sulfonation degree to the final acid uptake of the blends. As shown in Figure 4 an increase of the sulfonation degree results in higher doping levels.

This behavior was expected since in the SPSF(Na)₉₀ there are more sites (SO₃⁻) than in

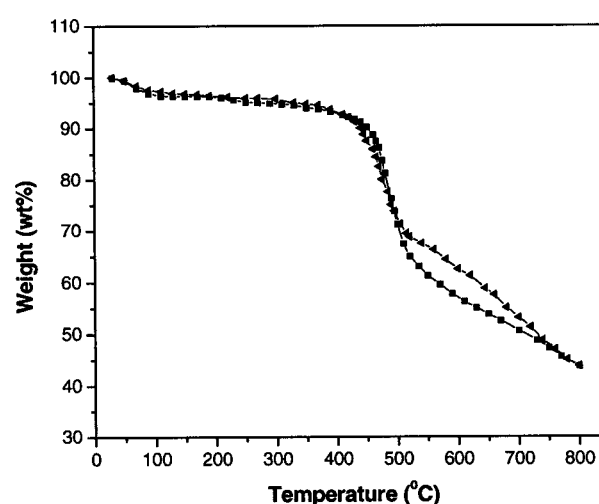


Figure 3. TGA thermogram of PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend before (—▲—) and after (—■—) treatment with H₂O₂

SPSF(Na)₇₀ or SPSF(Na)₄₅ that can interact and retain H₃PO₄. Moreover, the temperature dependence of doping level was studied for the PPy(50)coPSF/SPSF(Na)₇₀ 60/40 blend as shown in Figure 5. This blend reaches doping level as high as 160%–170% wt.

The ionic conductivity for the PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend was also measured as a function of the doping level, as shown in Figure 6. As expected, an increase on acid uptake of the membrane also results in an increase of the proton conductivity.

In addition, the temperature dependence of the conductivity for the PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend for different doping levels was examined. As shown in Figure 7, the proton conductivity of the blend was 2.8×10^{-3} S/cm at 130°C, for a doping level of

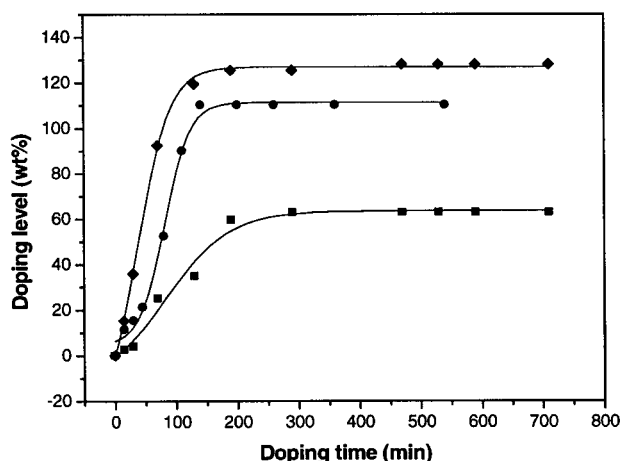


Figure 4. Time dependence of doping level (wt%) of PPy(50)coPSF/SPSF(Na)_x 75/25 blends for different sulfonation degrees: $x=45$ (-■-), $x=70$ (-●-), $x=90$ (-◆-) at 80°C

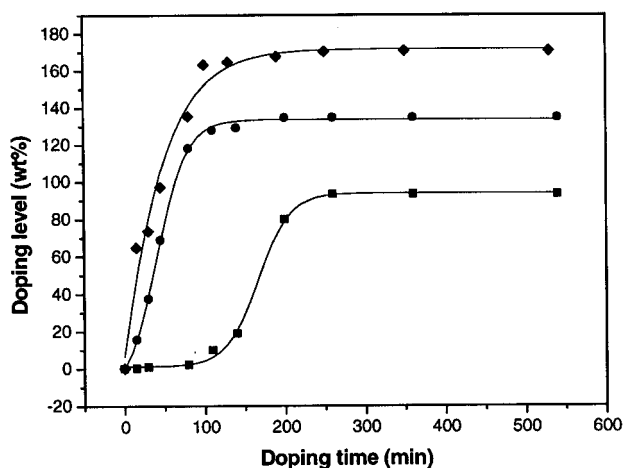


Figure 5. Time dependence of doping level (wt%) of PPy(50)coPSF/SPSF(Na)₇₀ 60/40 blend at 50°C (-■-), 80°C (-●-) and 100°C (-◆-)

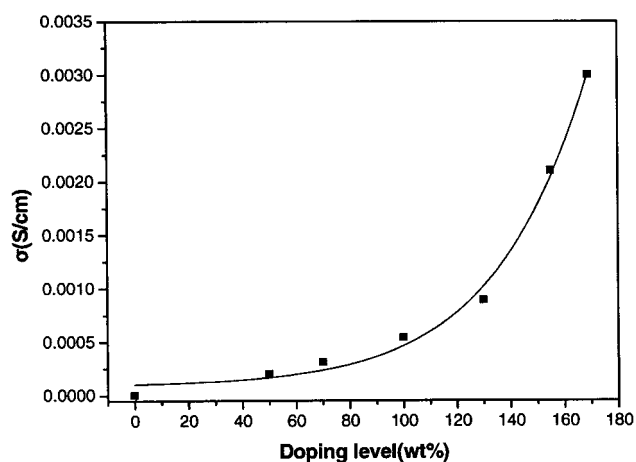


Figure 6. Doping level dependence of ionic conductivity of the PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend at room temperature

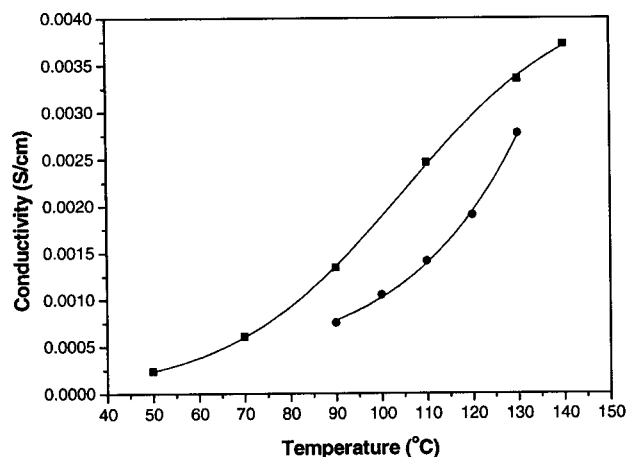


Figure 7. Temperature dependence of ionic conductivity of acid doped PPy(50)coPSF/SPSF(Na)₇₀ 75/25 with a doping level 100%wt (-●-) and 120%wt (-■-) H₃PO₄

100%wt while the proton conductivity for a doping level of 120%wt was $3,9 \times 10^{-3}$ S/cm at 140°C. As expected, the proton conductivity increases with the increase of temperature and doping level.

The activation energy (E_a) for the PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend was also calculated from the slope of the Arrhenius plot $\ln \sigma$ vs $1000/T$. As shown in Figure 8, for a doping level of 100%wt and 120%wt, the activation energy (E_a) was calculated 39 KJ/mol and 25 KJ/mol, respectively, showing a decrease of the E_a values as the doping level is increasing.

Finally, the PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend was selected as a candidate polymer electrolyte in PEMFCs due to its high proton conductivity and its good mechanical properties. The membrane showed good stability during the operation as well as acceptable performance. I-V curves at different operation temperatures are given in Figure 9. As shown there, an increase of the temperature results in an increase of the

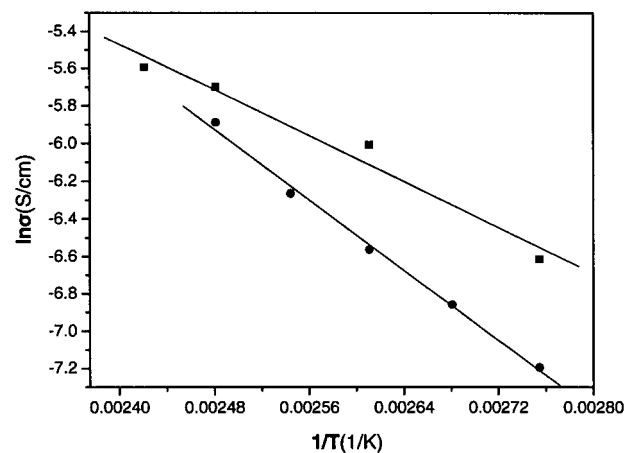


Figure 8. Temperature dependence of ionic conductivity of acid doped PPy(50)coPSF/SPSF(Na)₇₀ 75/25 with a doping level 100%wt and 120%wt H₃PO₄. Activation energy 39 KJ/mol (-●-) and 25 KJ/mol (-■-), respectively

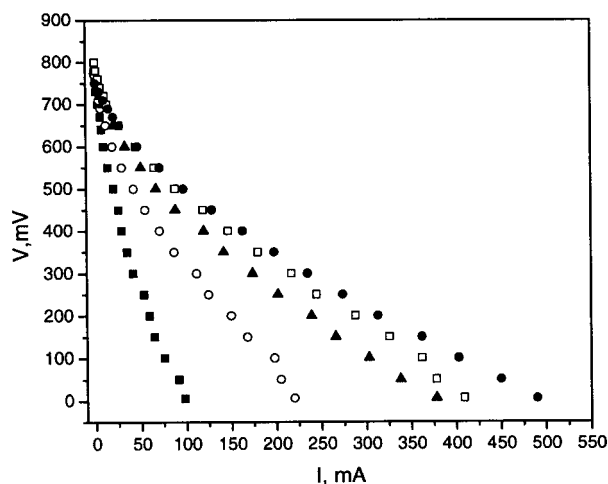


Figure 9. I-V curves of the PPy(50)coPSF/SPSF(Na)₇₀ 75/25 membrane for different temperatures: (—■—) 60 °C, (—○—) 80°C, (—▲—) 100°C, (—□—) 120°C, (—●—) 130°C for a 2x2 cm² single cell

conductivity, since it is obvious that the slope of the curve is decreased. Furthermore, increase of temperature improves the fuel cell performance. The current output is quite low but it should be noted that no optimization regarding the MEA has been performed so far. Different parameters involving the MEAs construction and the single cell operation conditions have to be improved in order to optimize the performance of the PEMFC.

CONCLUSION

Polymer membranes composed of PPy(50)coPSF/SPSF(Na)_x were prepared and studied in respect to their properties. In most cases blends with mechanical integrity, high oxidative and thermal stability and ionic conductivity in the range of 10⁻³ S/cm after doping with phosphoric acid were obtained. An initial single cell test of the PPy(50)coPSF/SPSF(Na)₇₀ 75/25 blend showed promising results, through an optimization.

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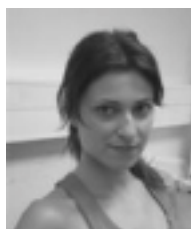
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REFERENCES

- [1] M.S. Dresselhaus, I.L. Thomas, Alternative energy technologies, *Nature* **414** (2001) 332–337
- [2] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, *Nature*, **414** (2001) 345–352
- [3] W.H.J. Hogarth, J.C. Diniz da Costa, G.Q. Max Lu, Solid acid membranes for high temperature (>140°C) proton exchange membrane fuel cells, *Journal of Power Sources* **142** (2005) 223–237
- [4] K.A. Mauritz and R.B. Moore, State of Understanding of Nafion, *Chem. Rev.* **104** (2004) 4535–4585
- [5] O. Savadogo, Emerging membranes for electrochemical systems Part II. High temperature composite membranes for polymer electrolyte fuel cell (PEFC) applications, *Journal of Power Sources* **127** (2004) 135–161
- [6] Y.-L. Ma, J.S. Wainright, M.H. Litt, R.F. Savinell, Conductivity of PBI Membranes for High-Temperature Polymer Electrolyte Fuel Cells, *Journal of The Electrochemical Society*, **151** (1) (2004) A8–A16
- [7] L. Qingfeng, R. He, J.O. Jensen, N.J. Bjerrum, Approaches and Recent Development of Polymer Electrolyte Membranes for Fuel Cells Operating above 100°C, *Chem. Mater.* **15** (2003) 4896–4915
- [8] M. Rikukawa, K. Sanui, Proton conducting polymer electrolyte membranes based on hydrocarbon polymers, *Prog. Polym. Sci.* **25** (2000) 1463–1502
- [9] J. Roziere, D.J. Jones, Non-Fluorinated Polymer Materials for Proton Exchange Membrane Fuel Cells, *Annu. Rev. Mater. Res.* **33** (2003) 503–555
- [10] J.A. Kerres, Development of ionomer membranes for fuel cells, *J. Membr. Sci.* **185** (2001) 3–27
- [11] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative Polymer Systems for Proton Exchange Membranes (PEMs), *Chem. Rev.* **104** (2004) 4587–4612
- [12] D.J. Jones, J. Roziere, Recent advances in the functionalisation of polybenzimidazole and polyetherketone for fuel cell applications, *J. Membr. Sci.* **185** (2001) 41–58
- [13] M. Gil, X. Ji, X. Li, H. Na, J.E. Hampsey, Y. Lu, Direct synthesis of sulfonated aromatic poly(ether ether ketone) proton exchange membranes for fuel cell applications, *Journal of Membrane Science* **234** (2004) 75–81
- [14] F. Lufrano, G. Squadrito, A. Patti, E. Passalacqua, Sulfonated Polysulfone as Promising Membranes for Polymer Electrolyte Fuel Cells, *J. Appl. Polym. Sci.*, **77** (2000) 1250–1257
- [15] F. Lufrano, I. Gatto, P. Staiti, V. Antonucci, E. Passalacqua, Sulfonated polysulfone ionomer membranes for fuel cells, *Solid State Ionics* **145** (2001) 47–51
- [16] C. Hasiotis, Li. Qingfeng, V. Deimede, J.K. Kallitsis, C.G. Kontoyannis, N.J. Bjerrum, *Journal of The Electrochemical Society*, **148** (5) (2001) A513–A519
- [17] V. Deimede, G.A. Voyiatzis, J.K. Kallitsis, L. Qingfeng, N.J. Bjerrum, *Macromolecules*, **33** (2000) 7609–7617
- [18] M.K. Daletou, N. Gourdoupi, J.K. Kallitsis, Proton conducting membranes based on blends of PBI with aromatic polyethers containing pyridine units, *J. Membr. Sci.* **252** (2005) 115–122
- [19] N. Gourdoupi, A.K. Andreopoulou, V. Deimede, J.K. Kallitsis, Novel proton-conducting polyelectrolyte composed of an aromatic polyether containing main-chain pyridine units for fuel cell applications, *Chem. Mater.* **15**(2003) 5044–5050
- [20] B.C. Jonson, I. Yilgor, C. Tran, M. Iqbal, J.P. Wightman, D.R. Lloyd, J.E. McGrath, *Journal of Polymer Science, Polymer Chemistry Edition*, **22** (1984) 721–737
- [21] B. Kosmala, J. Schauer, Ion-Exchange Membranes Prepared by Blending Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) with Poly-benzimidazole, *J. Appl. Polym. Sci.*, **85** (2002) 1118–1127
- [22] G. Hubner, E. Roduner, EPR investigation of HO* radical initiated degradation reactions of sulfonated aromatics as model compounds for fuel cell proton conducting membranes, *J. Mater. Chem.*, **9** (1999) 409–418
- [23] O. Olabisi, L.M. Robeson, M.T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York 1979

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