Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 104 (2005) 213–218

CATALYSIS TODAY

www.elsevier.com/locate/cattod

High temperature proton exchange membrane fuel cell using a sulfonated membrane obtained via H_2SO_4 treatment of PEEK-WC

Luca Paturzo [a,*], Angelo Basile [b,1], Adolfo Iulianelli [a],
Johannes C. Jansen [b], Irene Gatto [c,2], Enza Passalacqua [c]

[a] *Department of Chemical Engineering and Materials, University of Calabria, Via P. Bucci, 87030 Rende, CS, Italy*
[b] *Institute on Membrane Technology, ITM-CNR, c/o University of Calabria, Via P. Bucci, Cubo 17/C, 87030 Rende, CS, Italy*
[c] *CNR-ITAE, Advanced Technologies for Energy Institute, Via Salita S. Lucia sopra contesse 5, 98126 S. Lucia, Messina, Italy*

Abstract

A method for the sulfonation of PEEK-WC, a glassy poly(ether ether ketone) with sulphuric acid is presented. Depending on the reaction time, polymers with ion exchange capacity (IEC) from 0.30 to 0.76 $\text{meq}_{\text{H}^+}/\text{g}$ are obtained, as determined by titration with NaOH solutions. The thermal properties of the polymers were studied by differential scanning calorimetry, showing that the glass transition temperature increases with increasing degree of sulfonation, from 224 °C for pure PEEK-WC to 246 °C for the polymer having an IEC of 0.76 $\text{meq}_{\text{H}^+}/\text{g}$. The sulfonated polymers were used to prepare proton exchange membranes for possible application in fuel cells. Dense membranes were prepared by solvent evaporation, using DMA as the solvent. The transport properties of the membranes were determined in terms of water uptake and permeability for hydrogen and oxygen. Electrochemical characterization was performed by measuring cell voltage and power density curves as a function of current density at different working temperatures and the results were compared with those of a commercial Nafion membrane. A power density of 284 mW/cm^2 was obtained for S-PEEK-WC membrane at 120 °C in H_2/air fuel cell, slightly above the corresponding value found for Nafion.

Keywords: PEEK-WC; Sulfonation; Proton exchange membrane; Fuel cell; Hydrogen

---

1. Introduction

PEMFCs are attractive because of their ability to convert the chemical energy of a fuel (e.g. hydrogen) directly into electrical energy, with relatively high efficiency. The main component of a PEMFC is a dense proton-exchange membrane, able to promote proton diffusion from the anode to the cathode region. Nowadays, commercial PEMFCs are based on the Nafion™ membrane, and exhibit high performance at low temperature (80 °C) [1–3]. Some problems still remain and prevent the full commercialisation of PEMFCs at reasonable costs: the high cost of the membrane, the fuel crossover, the catalyst poisoning in the anode region (mainly due to CO), etc. [4–6]. To solve these problems an approach could be the development of thermostable polymers having a dense structure with low costs and able to work at higher temperature ($T > 100$ °C) to prevent catalyst poisoning. For these reasons several kinds of proton-exchange membranes have been studied recently: sulfonated poly (ether ether ketone) [7–9], sulfonated polysulfone [10–12], sulfonated polybenzimidazole [8,13], sulfonated poly-phenoxybenzoyl-phenylene [9], sulfonated polyphosphazene [14], sulfonated polyethersulfone with cardo [15], and also composite membranes, such as SiO_2 on polymeric support [16,17].

In this work, the sulfonation of PEEK-WC [poly(oxa-*p*-phenylene-3,3-phtalido-*p*-phenylenxoxa-*p*-phenylenexoxy-*p*-phenylene)] for the preparation of proton-exchange membranes for fuel cell applications at higher temperature is proposed. The starting PEEK-WC polymer is amorphous

---

* Corresponding author. Tel.: +39 0984 492011; fax: +39 0984 402103.
E-mail addresses: l.paturzo@unical.it (L. Paturzo), a.basile@itm.cnr.it (A. Basile), irene.gatto@itae.cnr.it (I. Gatto).
[1] Tel.: +39 0984 492013; fax: +39 0984 402103.
[2] Tel.: 39 090 624240; fax: +39 090 624247.

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.03.050

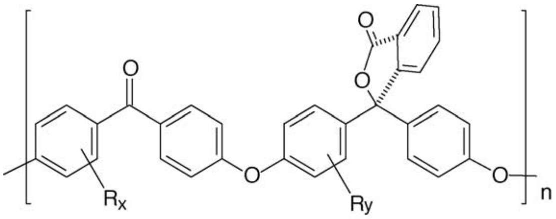

Fig. 1. Structure of the repeating unit of PEEK-WC (R = H, $x = y = 1$) and S-PEEK-WC (R = SO_3H, $x + y = 0.15–0.39$).

and exhibits high thermal and mechanical resistance [18]. It is soluble in different organic solvents such as $CHCl_3$, CH_2Cl_2, CH_2ClCH_2Cl, DMF, DMA, DMSO, THF. The structure of PEEK-WC is shown in Fig. 1. So PEEK-WC is suitable for the preparation of both porous (via a phase inversion technique induced by diffusion) and dense (via a phase inversion technique induced by a solvent evaporation) membranes. PEEK-WC can be chemically modified in order to achieve new materials for interesting applications. One example is the sulfonated PEEK-WC (S-PEEK-WC), which could present interesting properties in terms of proton conductivity due to proton transport in the polymeric matrix [18]. Responsible for the proton conductivity is the $–SO_3H$ group, which can be introduced in the PEEK-WC via a sulfonation reaction (Fig. 1). A pioneering work in this field has been done by Jia et al. [18], the only paper found in the literature regarding the sulfonation of PEEK-WC with H_2SO_4: these authors performed the sulfonation with concentrated H_2SO_4 (98%) in the temperature range of 40–60 °C. Their work shows good potential of sulfonated PEEK-WC in terms of proton-exchange properties, but it lacks an electrochemical investigation in order to establish the real potential in view of fuel cell applications. Recently, in order to obtain a dense membrane with good electrochemical performances, the PEEK-WC sulfonation was studied from another experimental point of view. In particular, sulfonation with chlorosulfuric acid has been tested, giving interesting results in view of direct methanol fuel cells application [19], both in terms of good proton conductivity and low methanol crossover, as compared to the commercial Nafion^{TM}117 membrane.

The aim of the present work is to check the potential of a sulfonated PEEK-WC membrane for higher temperature fuel cells (up to 120 °C). The sulfonation has been carried out with concentrated H_2SO_4, and the dense membrane has been characterised and tested in a fuel cell fed with H_2/air.

2. Experimental

2.1. PEEK-WC sulfonation

The PEEK-WC powder was supplied by the Changchun Institute of Applied Chemistry (Academia Sinica, China) and was used without further purification. Concentrated H_2SO_4 (96%) was purchased from Carlo Erba (Italy). The electrophilic aromatic sulfonation of PEEK-WC was performed by dissolving 50 g of the dry polymer in 500 ml of 96% H_2SO_4. A deep, red and viscous solution was obtained at the reaction temperature of 80 °C. Three different and consecutive fractions of polymer were isolated, after 1, 2, and 3 h of reaction time, respectively. The reaction was quenched by slowly pouring each viscous acidic fraction into 1 l of distilled water/ice mixture in order to consume the heat of dilution. The three sulfonated polymers were extensively washed with distilled water to remove the excess of acid, and dried in a vacuum oven at 60 °C and 5 mbar for one night. Both, the degree of sulfonation and the ion exchange capacity of the sulfonated polymers were determined and related to the reaction time.

2.2. Membrane preparation

The sulfonated polymer (S-PEEK-WC) was soluble in some organic solvents such as dimethylformamide, dimethylsulfoxide, dimethylacetamide (DMA), but insoluble in chloroform, differently from the mother polymer. For the membrane preparation, S-PEEK-WC was dissolved in DMA (33 wt.%) under stirring at room temperature for 24 h. The polymer solution was left under vacuum for 30 min in order to remove air bubbles from the solution, and cast onto a glass plate using a casting knife set at 250 μm. The membrane was dried at 30 °C for 8 h in a temperature-controlled oven under 5 mbar vacuum. Finally, the glass plate was put in a water bath in order to promote the release of the polymeric film. The resulting membrane was washed with distilled water and dried for 24 h at 40 °C under vacuum.

2.3. Chemical–physical characterisation

S-PEEK-WC and Nafion^{TM}117 reference sample (185 μm thick film) membranes were characterised in terms of ion-exchange capacity, dry gas permeation and water uptake. The thermal properties of S-PEEK-WC were also investigated.

2.3.1. Ion exchange capacity

A dry sample (0.50 g) of sulfonated polymer was weighed and thoroughly soaked in a 1 M NaCl solution to completely exchange the protons of the polymer. The released acid together with the swollen polymer was titrated with a 1.4×10^{-2}N aqueous NaOH solution by using an automatic titrator (Mettler DL21). The titration results have been used to calculate both the sulfonation degree (DS) and the ion exchange capacity (IEC). DS is defined as the number of $–SO_3H$ groups per repeating unit, while IEC is defined as the milliequivalents of H^+ per weight of dry polymer. DS has been calculated in an indirect mode from IEC data: formula (1) gives the calculation mode for DS

($MW_{\text{PEEK-WC monomer}} = 496.5$ g/mol; IEC is expressed in eq_{H^+}/g).

$$\begin{aligned} DS &= \frac{n_{SO_3H}}{n_{\text{PEEK-WC}}} \\ &= \frac{eq_{H^+} \times MW_{\text{PEEK-WC}}}{[m_{\text{sulfonated polyemr}} - (eq_{H^+} \times MW_{SO_3H})]} \\ &= \frac{IEC \times MW_{\text{PEEK-WC}}}{[1 - (IEC \times MW_{SO_3H})]} \end{aligned} \qquad (1)$$

where “*m*” indicates the mass of the species, “*n*” indicates the mole number, and MW is the molecular weight.

A similar equation was developed and used by Blanco et al. [15] for the calculation of DS from IEC in a sulfonated polyethersulfone cardo polymer.

2.3.2. Thermal properties

DSC measurements were carried out on a Pyris Diamond Differential Scanning Calorimeter (Perkin-Elmer) with a heating rate of 15 °C/min using samples of about 8 mg. The first run was stopped at 275 °C, the data were calculated from the second run.

2.3.3. Gas permeation tests

Dry gas permeation tests were performed by using a Permeability Testing Instrument (GKSS, Germany). The permeation test principle is based on a pressure increase measurement of the previously evacuated fixed volume permeate chamber. The attention has been focused on H_2 and O_2 permeation at room temperature (25 °C) for dense disk-shaped membrane samples (effective area 11 cm^2). Prior to each measurement series, the membrane was kept under vacuum for one night at slightly elevated temperature ($\geq$60 °C) to ensure complete removal of absorbed water.

2.3.4. Water uptake

Water uptake, defined in Eq. (2), was determined by immersing membrane samples in distilled water at a fixed temperature (25 and 80 °C) for 24 h; then, after quickly wiping off the excess water from the surface, they were weighed and put in oven at 80 °C under vacuum for 24 h in order to determine the dry weight.

$$\text{water uptake, } \% = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100 \qquad (2)$$

2.4. Electrochemical characterisation

The electrochemical characterisation was carried out in a 5 cm^2 commercial single cell (GlobeTech) connected to a Fuel Cell Technologies Test Station. The measurements were performed in the temperature range from 80 to 130 °C in H_2/air. Gas pressures of 3 bar abs were used with a constant gas flow of 1.5 and 2 times the stoichiometry at 1 A/cm^2 for hydrogen and air, respectively. The fuel cell test station was equipped with a humidifying system for the reactant gases. Humidifier temperatures were fixed at 10 °C (H_2) and 5 °C (air) higher than the cell temperature, except for the step at 130 °C, in which the humidifier temperature was the same as the cell temperature. The membrane–electrode-assemblies (MEAs) were prepared by using standard ELAT, with a Pt loading of 0.6 mg/cm^2 and a Nafion loading of 0.6 mg/cm^2. The cell resistance has been measured at open circuit voltage by using a Hewlett-Packard (type HP 4338B) milli-ohmmeter, that works at a frequency of 1 kHz. Electrochemical tests were carried out both on the S-PEEK-WC membrane and the Nafion^{TM}117 reference membrane in the same operative conditions.

3. Results and discussion

The three different polymer fractions obtained are referred to as: S-PEEK-WC-1h, S-PEEK-WC-2h, and S-PEEK-WC-3h, indicating 1, 2, and 3 h of reaction time, respectively. The sulfonation procedure led to the set of sulfonated polymers reported in Table 1. It is shown that increasing the reaction time both IEC and DS increase. The corresponding results for the Nafion^{TM}117 membrane are IEC = 0.93 meq_{H^+}/g and DS = 122.7%. A similar trend has been found by Jia et al. [18] for the PEEK-WC sulfonation but at lower sulfonation temperature. At 3 h of reaction time, a DS of about 40% has been achieved in this work operating at 80 °C, versus DS of 16 and 24% achieved by Jia et al. [18] operating at 40 and 60 °C, respectively. In the present work, the maximum reaction time of 3 h has been chosen due to a compromise between two phenomena occurring during the sulfonation and discussed by Jia et al. [18]. The first phenomenon is the increase in interaction among the polar –SO_3H groups, that leads to an increase of the polymer viscosity. The second one is the degradation of the chains, that leads to a reduction of the molar mass and thus of the polymer viscosity and film forming properties. This could result in a film of less mechanical stability and to defective membranes. There is a competition that gives an initial increase of the polymer viscosity up to 3 h of reaction time, followed by a dramatic decrease that makes the sulfonated polymers not suitable to prepare stable membranes. Polymers achieved in this work give stable membranes. However, with longer reaction times the membranes were found to become increasingly brittle upon complete drying,

Table 1
Properties of the three sulfonated polymers

Polymer type	IEC (meq_{H^+}/g)[a]	DS (%)[b]	T_g (°C)[c]
PEEK-WC	–	–	224
S-PEEK-WC-1h	0.30 ± 0.01	15.5 ± 0.5	n.d.
S-PEEK-WC-2h	0.55 ± 0.01	28.5 ± 0.4	239
S-PEEK-WC-3h	0.76 ± 0.02	39.9 ± 0.9	246
Nafion^{TM}117	0.93 ± 0.01	122.7 ± 0.2	~110 °C

[a] Average value and maximum semi-dispersion of five independent measurements on different sample specimens.

[b] Calculation performed according to Eq. (1), Section 2.3.1.

[c] Half C_p value.

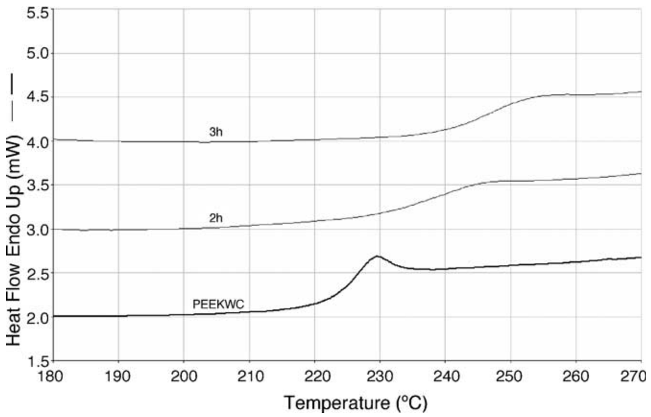

Fig. 2. DSC of the second heating run of PEEK-WC and S-PEEK-WC samples (15 °C/min).

which may indicate a partial degradation and loss of the molar mass of the polymers or a probable change of the intrinsic mechanical properties, depending on the degree of substitution. Due to the low IEC of the S-PEEK-WC-1h and S-PEEK-WC-2h only the S-PEEK-WC-3h powder has been used to prepare dense membranes to be tested in the hydrogen fuel cell.

Table 1 also shows the glass transition temperatures (half C_p value) of the two sulfonated samples S-PEEK-WC-2h and S-PEEK-WC-3h, in comparison with the mother polymer. T_g curves are presented in Fig. 2. The sulfonation causes a significant increase of T_g of about 15 °C for sample S-PEEK-WC-2h and about 22 °C for sample S-PEEK-WC-3h. This is probably due to the increased steric hindrance and to polar interactions between the relatively polar sulfonic acid groups. No melting peaks are detected, indicating the amorphous character of both the sulfonated and the mother polymer. A high T_g is desirable for applications of the sulfonated PEEK-WC in fuel cells that should operate at elevated temperatures, since it will guarantee a good dimensional stability of the membrane during operation of the fuel cell. In practice, however, the water present during normal operation of the fuel cell will plasticize the polymer and thus cause a somewhat lower T_g. This may be one of the reasons of the better performance of the sulfonated PEEK-WC at higher temperature in comparison with the Nafion$^{\mathrm{TM}}$117 reference membrane, as discussed below in Figs. 4 and 6. A heating run up to 275 °C did not show any indication of exothermal or irregular phenomena that can be ascribed to degradation reactions, indicating the polymer good thermal stability.

Dry gas permeability measurements were conducted on the S-PEEK-WC-3h membrane, prepared by using the sulfonated polymer S-PEEK-WC-3h (Table 1). The membrane thickness is 40 μm. Table 2 shows both H_2 and O_2 permeability at 25 °C for the S-PEEK-WC-3h membrane compared with some literature data regarding a PEEK-WC membrane [20]. The same table shows experimental (this work) and literature data [21,22] for the Nafion membrane.

Table 2
Dry gas permeability of sulfonated PEEK-WC and related polymers

Membrane type	P_{H_2}[a] (barrer)	P_{O_2}[a] (barrer)
S-PEEK-WC-3h	8.9	0.7
SP3101 [19]	6.4	0.4
PEEK-WC [20]	6.0	1.0
Nafion$^{\mathrm{TM}}$117 [this work]	5.8	1.3
Nafion$^{\mathrm{TM}}$117 [21]	4.3	–
Nafion$^{\mathrm{TM}}$112 [22]	–	0.9

[a] 1 barrer = 10^{-10} cm^3 (STP) cm/(s cm^2 cmHg)].

In order to compare the performance with sulfonated PEEK-WC membrane achieved via sulfonation with chlorosulfuric acid, the experimental data presented by Drioli et al. [19] were reported for a sulfonated PEEK-WC membrane (SP3101, DS = 70%) 77 μm thick. The comparison given in Table 2 shows that sulfonated PEEK-WC membranes exhibit permeability values quite similar to those related to the not-sulfonated ones, and also similar to those related to the Nafion$^{\mathrm{TM}}$117 membrane. Permeation tests are important in view of application of such membranes in a PEMFC, because low gas permeation corresponds to low crossover through the membrane and to a consequent high efficiency of the fuel cell. From the experimental results reported in Table 2 it is seen that both, H_2 and O_2 permeability of S-PEEK-WC-3h, are of the same order of magnitude of the PEEK-WC membrane: this suggests that the $-SO_3H$ groups insertion into the polymeric matrix does not influence so much the transport properties of the dense membrane toward these gases. Moreover, the H_2 and O_2 permeability is also within the same order of magnitude of the commercial Nafion$^{\mathrm{TM}}$117 membrane.

Table 3 shows the water uptake results at 25 and 80 °C of the proton-exchange membrane obtained with the sulfonated polymer S-PEEK-WC-3h. The commercial Nafion$^{\mathrm{TM}}$117 membrane was also tested and compared with some literature references. The water uptake of the S-PEEK-WC-3h membrane is about 14% at both temperatures, versus about 20 and 23% for the Nafion$^{\mathrm{TM}}$117 membrane at the same temperatures. These experimental results are important considering that the electrochemical performances of the membrane are correlated to its water retention capacity and also to the IEC value. In fact, both IEC and water uptake contribute to the proton transport through the dense membrane.

Fig. 3 shows the polarization curve in H_2/air of MEA prepared with the S-PEEK-WC-3h membrane, in the range

Table 3
Water uptake (wt.%) of the sulfonated PEEK-WC membrane compared to the Nafion$^{\mathrm{TM}}$117 membrane

Membrane type	$T = 25$ °C	$T = 80$ °C
S-PEEK-WC-3h	14	14
Nafion$^{\mathrm{TM}}$117 [this work]	20	23
Nafion$^{\mathrm{TM}}$117 [6]	–	27
Nafion$^{\mathrm{TM}}$117 [7]	35	–

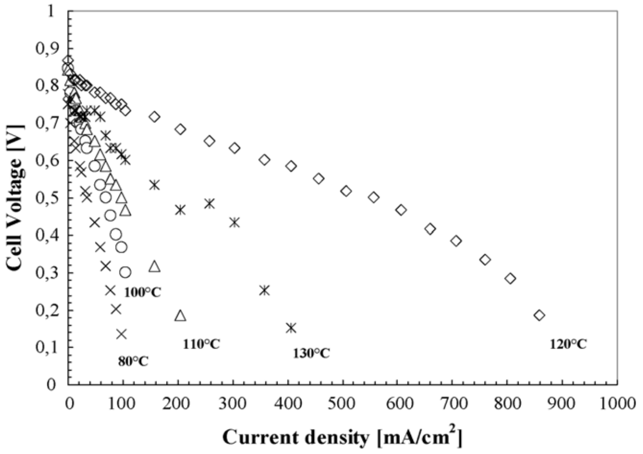

Fig. 3. Polarization curves for the S-PEEK-WC-3h membrane at different temperatures. H_2/air, T_{cell} = 80–130 °C, $P_{H_2} = P_{\mathrm{air}} = 3$ bar abs, 52 SCCM H_2, 175 SCCM air. Membrane thickness = 40 μm.

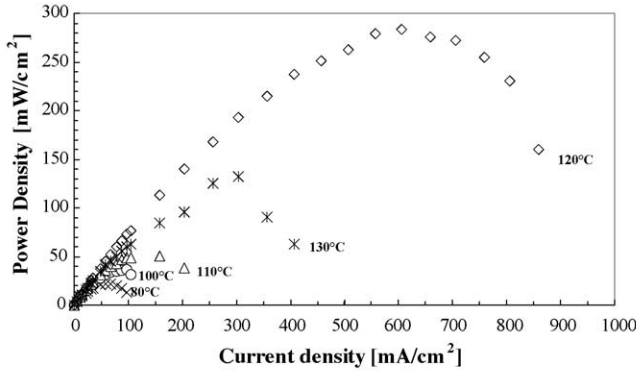

Fig. 5. Power density curves for the S-PEEK-WC-3h membrane at different temperatures. H_2/air, T_{cell} = 80–130 °C, $P_{H_2} = P_{\mathrm{air}} = 3$ bar abs, 52 SCCM H_2, 175 SCCM air. Membrane thickness = 40 μm.

of 80–130 °C. An increasing trend is seen with the increase of temperature, obtaining the best results at 120 °C, while Nafion membranes have optimal operation temperature at about 80 °C, as reported in literature [23,24]. The cell resistance decreases by increasing the temperature, and it is 0.240 Ω cm^2 at 120 °C, versus a value of 0.135 Ω cm^2 found for the MEA prepared with the Nafion$^{\mathrm{TM}}$117.

Fig. 4 shows a comparison of the polarization curves between the S-PEEK-WC-3h membrane and Nafion$^{\mathrm{TM}}$117 at 120 °C. The polarization curves have a similar behaviour until to 560 mA/cm^2, but the S-PEEK-WC-3h membrane has a higher limit current, about 900 respect to 700 mA/cm^2 obtained for the Nafion$^{\mathrm{TM}}$117. The lower cell voltage exhibited by the S-PEEK-WC-3h membrane in the low current density zone could denote the occurrence of parasitic reactions as pointed out by Lufrano et al. [11] for Nafion$^{\mathrm{TM}}$117 and sulfonated polysulfone membranes. Nevertheless, the behaviour in the high current density zone demonstrates that the S-PEEK-WC-3h membrane gives lower mass transport limitations with respect to the Nafion$^{\mathrm{TM}}$117 reference: this phenomenon could be attributed to the different thickness of the two membranes (40 μm for the S-PEEK-W-3h versus 185 μm for the Nafion$^{\mathrm{TM}}$117 membrane). The main consideration is so that the application of thin dense membranes to PEMFC is effective to achieve high performance. See, e.g., Liu et al. [25].

The power density curves for the S-PEEK-WC-3h membrane at different temperatures are shown in Fig. 5. The best performances were obtained at 120 °C, achieving 284 mW/cm^2 with a current density of about 600 mA/cm^2 at 0.5 V. In Fig. 6, the power density curves at 120 °C are reported. The maximum power density of 275 mW/cm^2 has been achieved for Nafion$^{\mathrm{TM}}$117 membrane, and 284 mW/cm^2 for the S-PEEK-WC-3h membrane. These results are very promising if we consider that they were obtained starting from a new, versatile and low cost material, that is the PEEK-WC polymer.

Further tests will be carried out to verify the stability of S-PEEK-WC-3h at high temperature and also the performances feeding the fuel cell with reformate hydrogen.

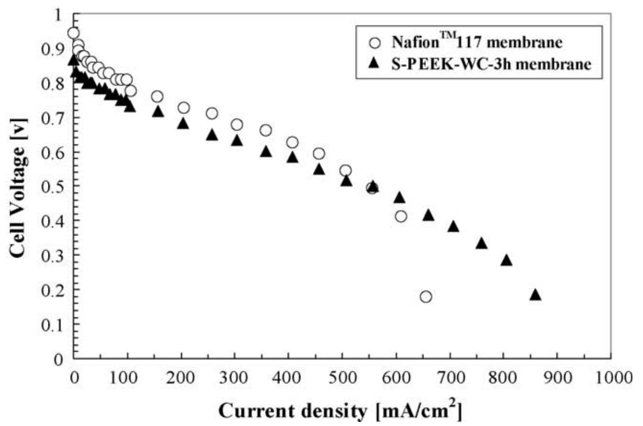

Fig. 4. Polarization curves at 120 °C: comparison between the S-PEEK-WC-3h and the Nafion$^{\mathrm{TM}}$117 membrane. H_2/air, $P_{H_2} = P_{\mathrm{air}} = 3$ bar abs, 52 SCCM H_2, 175 SCCM air. S-PEEK-WC-3h membrane thickness = 40 μm, Nafion$^{\mathrm{TM}}$117 membrane thickness = 185 μm.

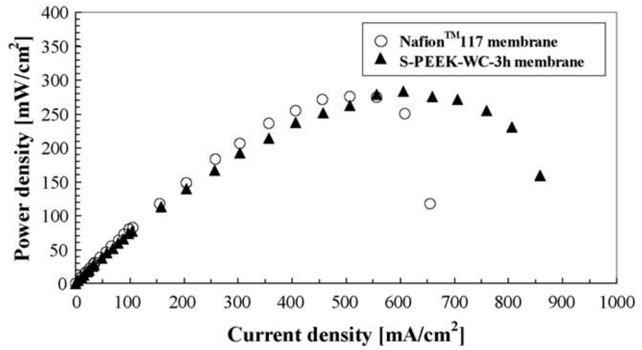

Fig. 6. Power density curve at 120 °C: comparison between the S-PEEK-WC-3h and the Nafion$^{\mathrm{TM}}$117 membrane. H_2/air, $P_{H_2} = P_{\mathrm{air}} = 3$ bar abs, 52 SCCM H_2, 175 SCCM air. S-PEEK-WC-3h membrane thickness = 40 μm, Nafion$^{\mathrm{TM}}$117 membrane thickness = 185 μm.

4. Conclusions

Sulfonation of PEEK-WC with concentrated (96%) H_2SO_4 was performed at 80 °C. Both the ion exchange capacity and the sulfonation degree can be influenced by the reaction time during sulfonation. Polymer with high DS is most suitable for the desired application: S-PEEK-WC-3h polymer having an IEC of 76 $\mathrm{meq_{H^+}/g}$ and DS of about 40% has been achieved after 3 h of reaction time. A 40 μm thick, dense membrane was prepared with the S-PEEK-WC-3h polymer. This membrane showed low dry gas (H_2 and O_2) permeation, which is favourable in view of PEMFC application since low gas crossover is expected to avoid efficiency loss of the fuel cell. About 14% of water uptake was achieved, and this property is important for the proton transport through the dense membrane during the fuel cell operation.

Electrochemical characterisation gives an optimum performance at 120 °C. A power density of 284 $\mathrm{mW/cm^2}$ was obtained for the S-PEEK-WC-3h membrane slightly above the value for Nafion$^{\mathrm{TM}}$117.

Sulfonation causes an increase of the glass transition temperature up to 246 °C, so the S-PEEK-WC-3h membrane seems to be quite promising for PEMFC application at higher temperatures (120 °C). In fact, one of the key aspects in the choice of the operating temperature of a PEMFC is the catalyst performance, especially the CO tolerance increases with increasing operating temperature. Moreover, if operating at higher temperature, it should be possible to increase the energy recovery from the produced water, in view of a combined energy production (electrical + thermal energy). In this way, the S-PEEK-WC-3h membrane seems to be promising for high temperature operation in PEMFC.

Acknowledgement

Authors wish to thank the Director of the CNR-ITAE Institute (Messina, Italy), Dr. Eng. Gaetano Cacciola, for the cooperation between our Institutes.

References

[1] L. Carrette, K.A. Friedrich, U. Stimming, Fuel Cells 1 (2001) 5–39.

[2] M. Wakizoe, O.A. Velev, S. Srinivasan, Electrochim. Acta 40 (3) (1995) 335–344.

[3] J.A. Kerres, J. Membr. Sci. 185 (2001) 3–27.

[4] F. Barbir, T. Gómez, Int. J. Hydrogen Energy 21 (10) (1996) 891–901.

[5] T. Schultz, S. Zhou, K. Sundmacher, Chem. Eng. Technol. 24 (2001) 1223–1233.

[6] L.J. Pettersson, R. Westerholm, Int. J. Hydrogen Energy 26 (2001) 243–264.

[7] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, J. Membr. Sci. 185 (2001) 73–81.

[8] D.J. Jones, J. Rozière, J. Membr. Sci. 185 (2001) 41–58.

[9] T. Kobayashi, M. Rikukawa, K. Sanui, N. Ogata, Solid State Ionics 106 (1998) 219–225.

[10] F. Lufrano, G. Squadrito, A. Patti, E. Passalacqua, J. Appl. Polym. Sci. 77 (2000) 1250–1257.

[11] F. Lufrano, I. Gatto, P. Staiti, V. Antonucci, E. Passalacqua, Solid State Ionics 145 (2001) 47–51.

[12] P. Genova-Dimitrova, B. Baradie, F. Foscallo, C. Poinsignon, J.Y. Sanchez, J. Membr. Sci. 185 (2001) 59–71.

[13] P. Staiti, F. Lufrano, A.S. Aricò, E. Passalacqua, V. Antonucci, J. Membr. Sci. 188 (2001) 71–78.

[14] R. Wycisk, P.N. Pintauro, J. Membr. Sci. 119 (1996) 155–160.

[15] J.F. Blanco, Q.T. Nguyen, P. Schaetzel, J. Membr. Sci. 186 (2001) 267–279.

[16] I. Honma, S. Nomura, H. Nakajima, J. Membr. Sci. 185 (2001) 83–94.

[17] P. Staiti, A.S. Aricò, V. Baglio, F. Lufrano, E. Passalacqua, V. Antonucci, Solid State Ionics 145 (2001) 101–107.

[18] L. Jia, X. Xu, H. Zhang, J. Xu, J. Appl. Polym. Sci. 60 (8) (1996) 1231–1237.

[19] E. Drioli, A. Regina, M. Casciola, A. Oliveti, F. Trotta, T. Massari, J. Membr. Sci. 228 (2004) 139–148.

[20] W.Y. Liu, T.L. Chen, J.P. Xu, J. Membr. Sci. 53 (3) (1990) 203–213.

[21] S. Hietala, E. Skou, F. Sundholm, Polymer 40 (1999) 5567–5573.

[22] K.M. Nouel, P.S. Fedkiw, Electrochim. Acta 43 (1998) 2381–2387.

[23] G. Alberti, M. Casciola, Ann. Rev. Mater. Res. 33 (2003) 129–154.

[24] J. Rozière, D.J. Jones, Ann. Rev. Mater. Res. 33 (2003) 503–555.

[25] F. Liu, Y. Baolian, X. Danmin, Y. Jingrong, Z. Huamin, J. Membr. Sci. 212 (2003) 213–223.