Preparation and characterization of sulfonated PEEK-WC membranes for fuel cell applications
A comparison between polymeric and composite membranes

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Abstract

Sulfonated poly(etheretherketone) with a cardo group (SPEEK-WC) exhibiting a wide range of degree of sulfonation (DS) was used to prepare polymeric membranes and composite membranes obtained by incorporation of an amorphous zirconium phosphate sulfophenylenphosphonate ($Zr(HPO_4)(O_3PC_6H_4SO_3H)$, hereafter Zr(SPP)) in a SPEEK-WC matrix. The nominal composition of the composite membranes was fixed at 20 wt% of Zr(SPP). Both types of membrane were characterized for their proton conductivity, methanol permeability, water and/or methanol uptake, morphology by SEM and mechanical properties. For comparison, a commercial Nafion 117 membrane was characterized under the same operative conditions. The composite membranes exhibited a reduced water uptake in comparison with the polymeric membranes especially at high DS values and temperature higher than 50 °C. As a result, the water uptake into composite membranes remained about constant in the range 20–70 °C. The methanol permeability (P) of both polymeric and composite membranes was always lower than that of a commercial Nafion 117 membrane. At 22 °C and 100% relative humidity (RH), the proton conductivities (σ) of the polymeric membranes increased from 6×10^{-4} to 1×10^{-2} S cm^{-1} with the increase of DS from 0.1 to 1.04. The higher conductivity value was comparable with that of Nafion 117 membrane (3×10^{-2} S cm^{-1}) measured under the same operative conditions. The conductivities of the composite membranes are close to that of the corresponding polymeric membranes, but they are affected to a lesser extent by the polymer DS. The maximum value of the σ/P ratio (about 7×10^4 at 25 °C) was found for the composite membrane with DS = 0.2 and was 2.5 times higher than the corresponding value of the Nafion membrane.
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1. Introduction

Fuel cells, and in particular the proton exchange membrane fuel cells (PEMFC), are an attractive power-generation technology that allows to generate electricity by direct electrochemical conversion of a fuel and an oxidant with both a low pollution level emission and a higher efficiency with respect to other traditional conversion systems [1–3].

Nowadays, the commercial available membranes are perflurosulfonic acid polymer based, such as Nafion from Du Pont, that still dominates the market because of its high proton conductivity and high chemical and mechanical stability. However, Nafion suffers from several drawbacks like its high cost, a loss of proton conductivity above 80 °C for the difficulty to maintain fully hydrated membrane [4], high methanol crossover, which hinders an effective application in a fuel cell directly fed with methanol (DMFC). The methanol crossover during operation leads to an efficiency reduction down 35% [5]. In the last decade, the preparation of inexpensive membranes based on nonfluorinated ionomers as alternative to Nafion has received much attention [6,7]. A certain number of poly-

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mer families such as polyphosphazenes, polybenzimidazole, polyethersulfone, poly(etherketone)s, etc., were used to prepare membranes for fuel cell applications. The majority of these polymers were sulfonated in order to realize membranes with high proton conductivity. In other cases a blend or cross-linked polymers to improve the performances of the membranes in terms of a higher conductivity, a lower fuel permeability or higher mechanical and chemical stability, respectively, have been used [4,8]. However, in the last years the investigation of different variants of sulfonated polyetherketones has been described in literature: polyetherketone (SPEK), poly(etheretherketone) [4,9–12] (SPEEK), poly(etherketoneketone) [13] (SPEKK), poly(etheretherketoneketone) [14] (SPEEKK) and a modified SPEEK having a cardo group on the backbone [15] (SPEEK-WC). The reason of this interest is that the membranes based on polyetherketones show a good chemical and mechanical stability, high proton conductivity, and both a reduced methanol permeability and a lower cost with respect to those of the Nafion membrane. The physical and chemical properties such as proton conductivity are affected by degree of sulfonation (DS) of the polymer.

In a previous paper we have described the preparation of SPEEK-WC membranes with a narrow range of DS and their characterization mainly in terms of proton conductivity and permeability to various gases, methanol and water [15]. All permeability measures were carried out on dry membranes and the results were compared to those of the Nafion obtained in the same operative conditions. Since the major properties of the membranes depend on their DS, in this work a particular attention has been focused on preparation and characterization of SPEEK-WC membranes with a wider range of DS. Besides, in order to improve the proton conductivity especially for the membranes at lower DS, new composite membranes by incorporation of a gel amorphous zirconium phosphate sulfophenylenphosphonate [$Zr(HPO_4)(O_3PC_6H_4SO_3H)$, hereafter Zr(SPP)] in SPEEK-WC polymeric matrix have been prepared. It has been reported that for analogous systems, the proton conductivity of a composite $Zr(HPO_4)_{0.7}(SPP)_{1.3}$/SPEK membrane can be an order of magnitude higher as compared to a pure SPEK membrane [16]. Then, Silva et al. [5] reported that the methanol and water permeability through the composite SPEEK/ZrPh/PBI with both various DS and composition were lower if compared to pure SPEEK membranes. Analogously, Nunes et al. [17] found composite SPEEK/$Zr(HPO_4)_2$/ZrO_2 membranes were less permeable to methanol and water with respect to polymeric membranes. Therefore, if these trends were maintained the new composite membranes prepared in this work could be promising in DMFC applications.

2. Experimental

2.1. Materials

Poly(oxa-*p*-phenylene-3,3-phtalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (PEEK-WC) was received from ChanChung Institute of Applied Chemistry (Academia Sinica, China). Sulfonated PEEK-WC (hereafter SPEEK-WC) was

obtained as described in Ref. [15]. The gel of 5.7 wt% Zr(SPP) in DMF was prepared according to Ref. [16].

2.2. Membrane preparation

Polymeric and composite membranes were prepared via the following procedures:

(i) For the polymeric membranes, a 27 wt% polymer solution in DMF was prepared by stirring overnight with a magnetic stirrer at room temperature. The solution was cast onto glass plate using a Gardner knife and cast films were subsequently slowly dried in thermostatic box at 20 °C and 20% relative humidity for 2 days. Then, the SPEEK-WC membranes were peeled of in a water bath at room temperature and dried at 60 °C in an oven for 24 h. After, the membranes were immersed in a 2 M HCl solution for 7 h and finally rinsed with distilled water up to pH 7.

(ii) For the composite membranes preparation, a 27 wt% SPEEK-WC solution in DMF was mixed with a suitable amount of the Zr(SPP) gel in DMF in order to obtain 20 wt% loading of Zr(SPP) in the membrane. This loading allows to obtain membranes with good performances in terms of proton conductivity and mechanical properties. The mixture was sonicated under stirring for 20 min, stirred over night at room temperature and finally cast on glass plate. The resulting film was dried at 20 °C and 20% of RH for 2 days, peeled of in distilled water bath, and then dried at 60 °C for 24 h. The membrane was immersed in a 2 M HCl solution for 7 h at room temperature and then washed several times with distilled water up to neutrality. The membrane was finally dried at 80 °C for 24 h.

2.3. Microscopic analysis

The membrane morphology was investigated by field emission scanning electron microscopy in a QUANTA 200F FEI, PHILIPS Instruments, using both secondary and backscattered electron detectors. The samples were fractured in liquid nitrogen and sputtered with gold in a penning sputtering equipment.

2.4. Mechanical properties

The tensile strengths of the membranes were measured using a Z2.5, Zwick Roell, Germany, and the test data were elaborated by the TestXpert V11.0 Master software. The size of specimen was of 15 mm × 3 mm, and the test speed was of 2 mm min^{-1}. Before the test, the membranes were immersed in water for about 3 h. For each testing reported, at least four specimens were taken and an average value was calculated. For a direct comparison between these and other data reported in literature, also a Nafion 117 commercial membrane was tested. In this case, instead, the test speed was fixed at 2 mm min^{-1} to determine Young's modulus (or tensile modulus) and then at 30 mm min^{-1} to determine the tensile strength and elongation at break, because the Nafion membrane is characterized by a high plasticity.

2.5. Swelling measurements

The membrane was dried at 70 °C for 24 h before measuring the dry membrane weight. Then, the membrane was soaked in water, or pure methanol at a fixed temperature for 12 h to promote full swelling. After, the membrane was wiped to remove any trace of liquid on the surface. Immediately, the weight of the swollen membrane was measured. The liquid uptake content was defined by:

$$SW(\%) = \left(\frac{W_{wet} - W_{dry}}{W_{dry}} \right) \times 100 \tag{1}$$

where W_{wet} and W_{dry} are the weight of swollen and dry membrane, respectively. The swelling measurements were carried out from room temperature up to 90 °C.

2.6. Methanol permeability measurements

Measurements of methanol permeation were carried out by the apparatus shown in Fig. 1. The equipment consisted of a glass diffusion cell (DC) with two compartments (semi-cells A and B) and a reservoir (R). The reservoir (400 mL) contained a 10 vol.% aqueous methanol solution (about 2.5 M). Semi-cell (B) contained ultra pure water (32 mL). The methanol solution was continuously flowed in the other semi-cell (A) from the reservoir, with a rate of 2.62 mL s^{-1} through a closed circuit by a peristaltic pump (P) (Masterflex model no 7521, Cole-Parmer Instruments, USA). This flow rate allowed a complete replacement of the methanol solution in about 12 s in order to maintain the methanol concentration homogeneous and constant in time. The solution homogeneity in the compartment (B) was maintained by a laboratory stirrer (St). The diffusion cell and the reservoir were immersed in a thermostatic bath in order to carry out the tests at various temperatures. The effective area of the membrane placed between the two compartments was 6.6 cm^2. The methanol concentration was monitored by using a gas chromatograph (Agilent Technologies Inc., mod. 6890N, USA) equipped with a PORAPAQ Q column, TCD detector, and injecting 1 μL of the sample solution for each determination in

the range of 2–5 h, depending on methanol permeation rate. The methanol permeability was obtained using the following relationship [18]:

$$C_B(t) = \left(\frac{PC_A A}{V_B L} \right) \left(\frac{t - L^2}{6D} \right) \tag{2}$$

where C_A and $C_B(t)$ (expressed in wt%) are the methanol concentration in the compartment A and methanol concentration in the water compartment B, at time t (s), respectively, P the permeability coefficient for methanol (cm^2 s^{-1}), V_B the volume of compartment B (cm^3), L the thickness of the membrane (cm), A the effective area of the membrane (cm^2) and D is the methanol diffusion coefficient. The permeability, P, can be directly determined by the slope of the plot of ($C_B(t) V_B L/A C_A$) versus time.

2.7. Conductivity measurements

The proton conductivity of each membrane was determined by ac impedance spectroscopy using an impedance/gain phase analyzer (Solarton 1260, Solartron Analytical, UK) in the frequency range from 1 Hz to 10 MHz, at a signal amplitude of 100 mV. The impedance data were corrected for the contribution of the open and the short-circuit cell and analyzed by the Zplot software (Scribner Associates Inc., USA). Before the test, the membrane (disc with $\phi = 9$ mm) was soaked in water for at least 10 h and then wiped on surface. Then, the sample was placed in a temperature controlled cell, where it was clamped between two porous stainless steel electrodes [19]. The design of the cell is similar to that already described by Alberti et al. [20]. The conductivity of the samples in the transverse direction was calculated from the impedance data, using the following relationship:

$$\sigma = \frac{d}{RS} \tag{3}$$

where σ is the conductivity (S cm^{-1}), d (cm) and S (cm^2) are the thickness and face area of the sample, respectively, and R (Ω) is the sample resistance derived from the high frequency intersection of the impedance diagram (reactance versus resistance) with the resistance axis.

3. Results and discussion

Polymer membranes of SPEEK-WC with a wide range of degree of sulfonation were prepared and characterized. The composite membranes were prepared with only three kinds of polymers (with low, medium and high DS value, respectively), and a fixed Zr(SPP) loading of 20 wt%. The Scheme 1 shows the chemical formula of SPEEK-WC and structural model for Zr(SPP). The summary of the abbreviations and characteristics of the membranes prepared in this work are reported in Table 1.

3.1. Micromorphology of the membranes

SEM analysis has shown that all the SPEEK-WC polymeric membranes are both dense and homogeneous since the surface
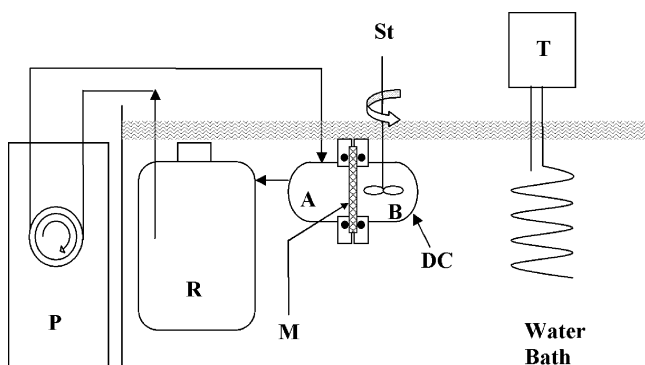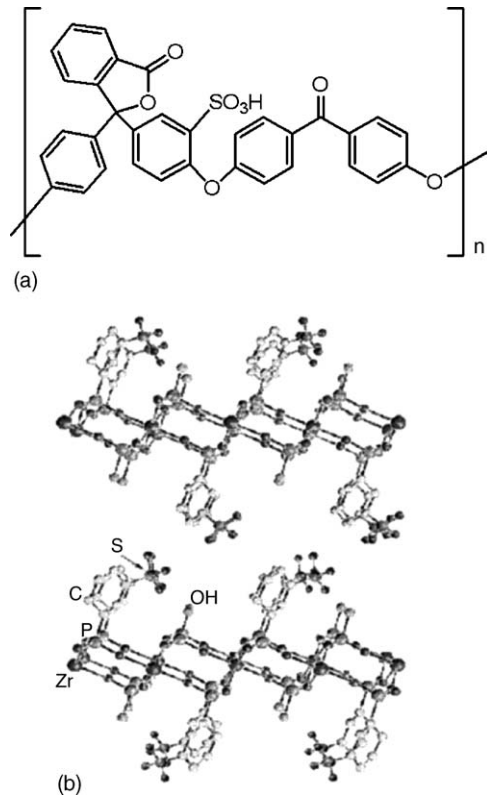

Fig. 1. Schematic diagram of the apparatus used for methanol permeation measurements. DC, diffusion cell; A, methanol solution compartment; B, water compartment; M, membrane; P, peristaltic pump; R, reservoir of the aqueous methanol solution; T, temperature controller of the water bath; St, laboratory stirrer.

(a)

(b)

Scheme 1. (a) Repeating monomer unit of sulfonated poly(oxa-*p*-phenilene-3.3-phtalido-*p*-phenilene-oxy-phenilene) (PEEK-WC). (b) Structural model for amorphous zirconium phosphate sulfophenylenphosphonate [$Zr(HPO_4)(O_3PC_6H_4SO_3H)$].

Table 1
Summary of the characteristics of the polymeric and composite membranes described in this work

Membrane (abbreviation)	DS	Nominal composition [wt% Zr(SPP)/(Zr(SPP) + SPEEK-WC)]	Thickness (μm)
SP10	0.10	–	80
SP20	0.20	–	95
SP38	0.38	–	92
SP57	0.57	–	95
SP80	0.80	–	77
SP104	1.04	–	58
ZrSP20	0.20	20	55
ZrSP57	0.57	20	57
ZrSP104	1.04	20	55

a few branched domains. The absence of significant contrast in the BSE image (Fig. 3) indicates that these domains cannot be identified with filler particles or filler rich regions. Therefore, no aggregate of grains is formed during membrane preparation and the size of each grain lies certainly below 100–200 nm as reported by Alberti et al. [16] for similar systems.

3.2. Mechanical properties

In order to evaluate the mechanical properties of the membranes, Young's modulus (or tensile modulus), yield stress and elongation at break (%) were measured and compared to those of a commercial Nafion 117 membrane. Fig. 4 shows the Young's modulus of both the polymeric and composite membranes as a function of the DS. It can be observed that the Young's modulus decreases from about 800 to 550 MPa when DS increases from 0.1 to 1.04 for polymeric membranes, while it does not depend on DS for the composite membranes in the range investigated. The Young's modulus of the commercial Nafion 117 membrane is lower than that SPEEK-WC based membranes. Fig. 5 shows the yield stress as a function of DS for both the polymeric and com-
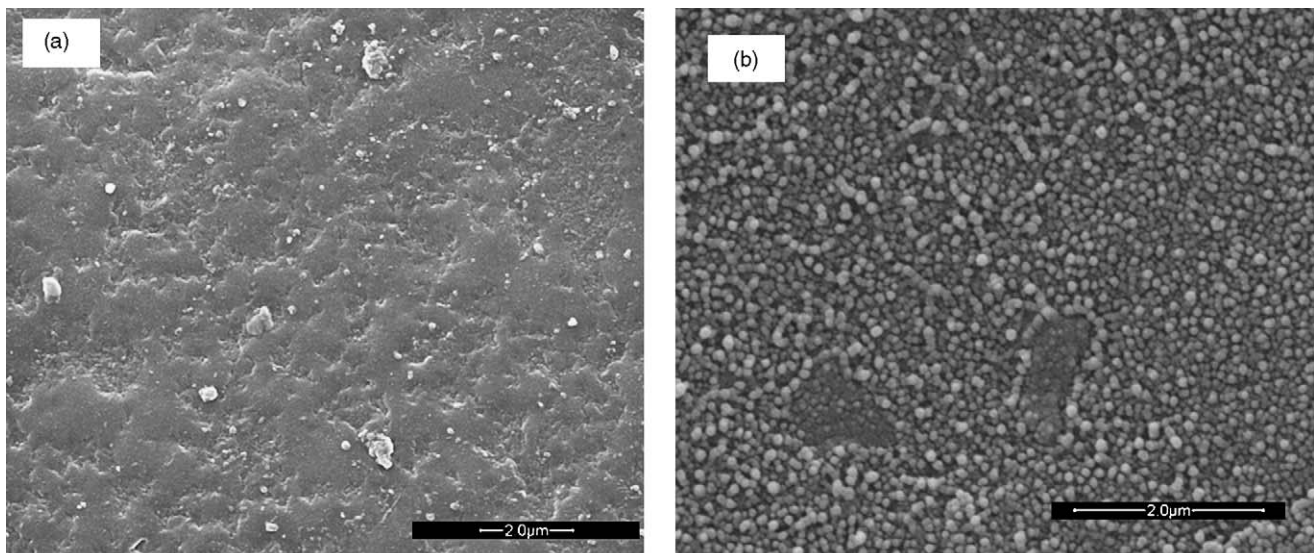
is smooth and there is not evidence of defects such as holes, porosity or surface cracks. In Fig. 2, SEM images of the surface and the cross-section of the composite ZrSP104 membrane with DS = 1.04 are shown. In Fig. 2a, a rough surface can be observed, while the membrane section (Fig. 2b) exhibits light grey globular domains, with average size around 200 nm, together with

Fig. 2. SEM images of the ZrSP104 composite membrane: (a) surface (20,000×) and (b) cross-section (20,000×).
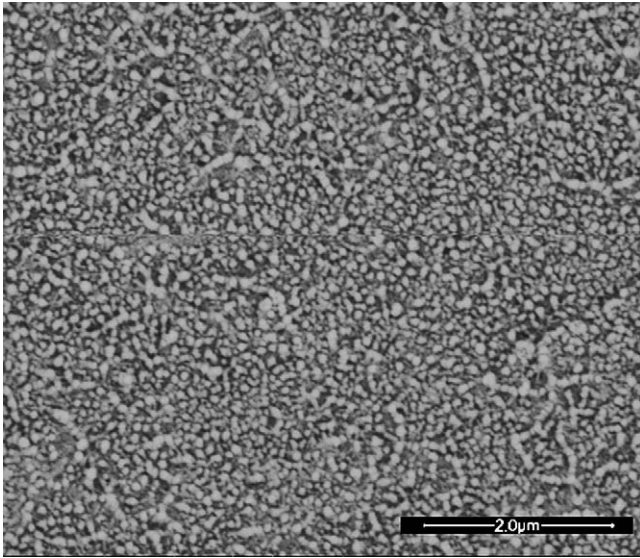
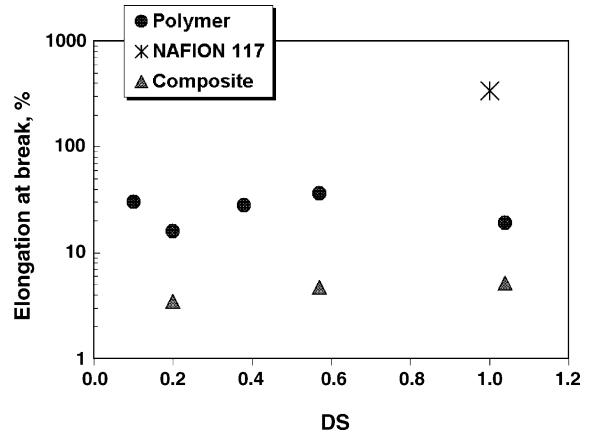Fig. 3. BSE image of the cross-section of the ZrSP104 composite membrane (20,000×, magnification).

Fig. 6. Elongation at break vs. degree of sulfonation of the polymers.

the maximum stress at break is 25 MPa in agreement with literature data, where is reported 27 MPa [21]. Fig. 6 shows that the elongation at break (%) of the composite membranes is on average one order of magnitude lower than that of the polymeric membranes, being in both cases nearly independent of DS. In comparison to the Nafion 117 membrane, the elongation at break of the polymeric membranes results lower by one order of magnitude. Therefore, the results of mechanical tests show that all the SPEEK-WC based membranes are harder and more brittle with respect to Nafion 117 membrane.

3.3. Liquid uptake

Many properties of SPEEK membranes depend on the degree of sulfonation. A higher DS value increases the hydrophilic character of the membrane and then the water amount absorbed [14]. Fig. 7 shows water absorption into SPEEK-WC polymeric membranes as a function of temperature for different DS values. It can be observed that at room temperature the uptake increases from about 8 to 60% when the DS value increases from 0.20 to 1.04. The water uptake percentage remains almost constant in the temperature range investigated for membranes with DS $\leq$ 0.57, while increases slightly with temperature for the membrane with DS = 0.80. However, for membrane with
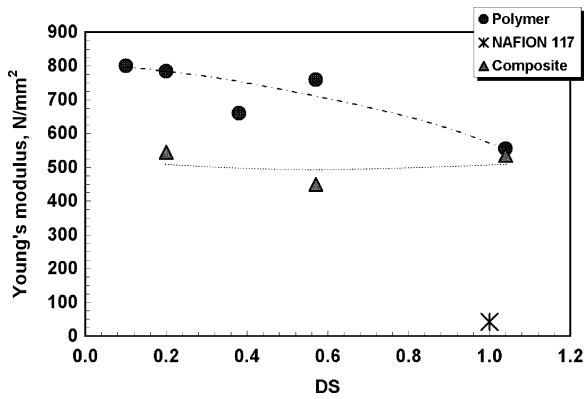

Fig. 4. Young's modulus as a function of the DS for polymeric and composite membranes. For a comparison Young's modulus of the Nafion 117 membrane has been reported. It is indicated arbitrary DS = 1 for Nafion 117.

posite membranes compared to Nafion 117 membrane. It can be observed that the yield stress values significantly decrease with the DS of about 50% for polymeric membranes, while they keep constant for composite membranes. For Nafion 117 membrane
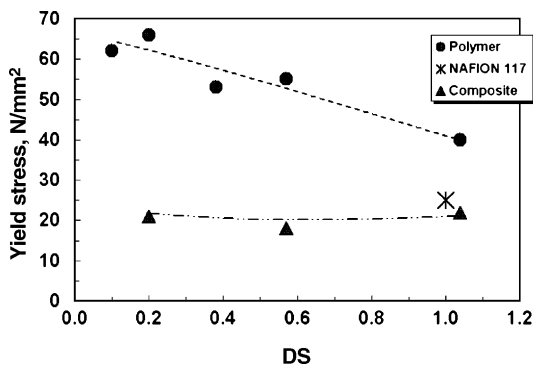

Fig. 5. Yield stress as a function of DS of the polymeric and composite membranes. For Nafion 117 membrane it has been reported the stress at breaking point.
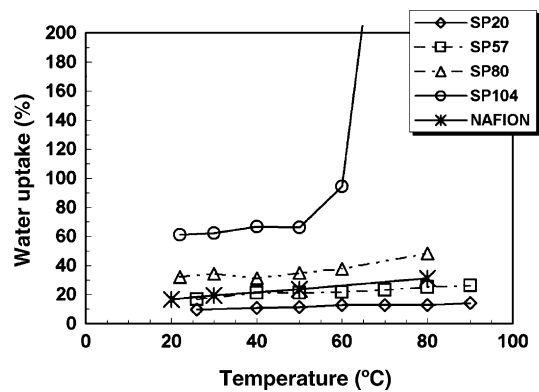

Fig. 7. Water uptake as a function of temperature for SPEEK-WC membranes with different degree of sulfonation. The uptake of a commercial Nafion 117 membrane has been reported as a reference.
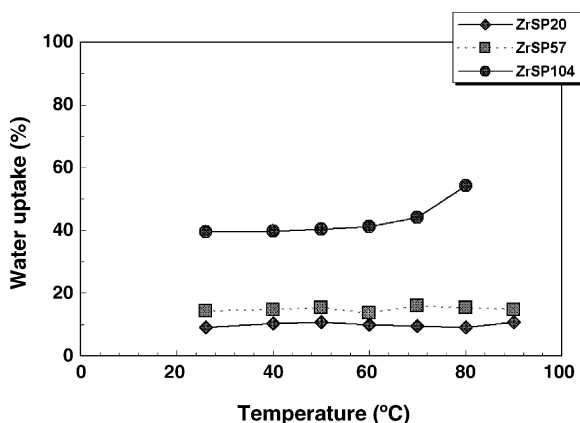
Fig. 8. Water uptake as a function of temperature for composite Zr(SPP)/SPEEK-WC membranes made of polymers with different DS values.

higher DS (e.g. DS = 1.04) there is an abrupt increase in water uptake, up to 500% at $T = 80\,°C$, corresponding to an irreversible deformation. This last aspect is a drawback for a possible use of these membranes in fuel cells because it may cause mechanical membrane failure during operation. The uptake of the commercial Nafion 117 membrane is comparable with that of SP57 and increases linearly with the temperature reaching 31% at 80 °C. Fig. 8 shows the water uptake as a function of temperature for Zr(SPP)/SPEEK-WC composite membranes made of polymers with different DS values. It can be observed that at room temperature the water uptake increases with DS, but to a lesser extent than for the corresponding polymeric membranes. At 80 °C, the water uptake for composite ZrSP104 membrane is 56% versus about 500% for the corresponding SP104 polymeric membrane (see Fig. 7). The reduced swelling at temperatures up to 80 °C represents an essential advantage in the fuel cell applications, especially in DMFC, because it can reduce the electroosmotic drag [22], methanol permeation, and it allows to maintain a good membrane-electrode contact. Fig. 9 shows the pure methanol uptake into polymeric and composite membranes, respectively, as a function of the temperature. For a comparison also the pure methanol uptake of the Nafion 117 has been reported. It can be observed that for temperatures up to 50 °C the uptake is about the same for all membranes, and it is lower than that of
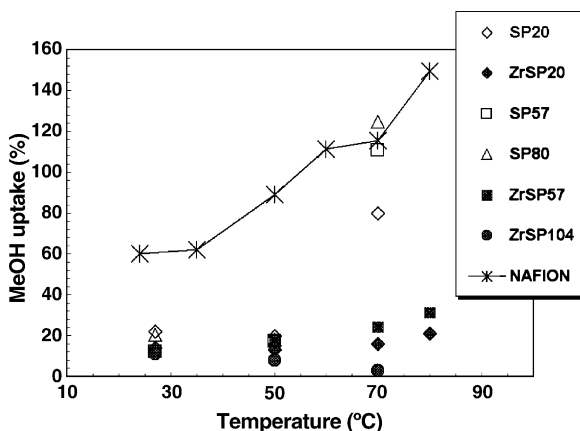
Nafion. With increasing the temperature up at 70 °C, the uptake of the polymeric membranes become very high, while it is almost constant for the composite ones. Increasing further the temperature a partial solubility of the polymeric membranes and of ZrSP104 composite membrane has been observed. For the composite membranes with a lower DS value, the swelling slightly increases.

3.4. Methanol permeability

Prior to methanol permeability measurements, all membrane samples were soaked in water for a full hydration. The measurements were carried out in the temperature range 25–53 °C. The apparatus for permeability tests was calibrated measuring the methanol permeation rate through a commercial Nafion 117 membrane. From these experiments the methanol permeability at 25 °C turned out to be 1.2×10^{-6} ($cm^2\,s^{-1}$) which is a value similar to those previously reported in literature: 1.98×10^{-6} ($cm^2\,s^{-1}$) at 25 °C and a feed concentration of 2.0 M methanol [18], $(1–1.5) \times 10^{-6}$ ($cm^2\,s^{-1}$) at 22 °C and 2.0 M methanol [23], 1×10^{-6} ($cm^2\,s^{-1}$) at 25 °C and 5 M methanol [24] and 1.72×10^{-6} ($cm^2\,s^{-1}$) at 25 °C and 2 M methanol [25].

Fig. 10 shows the methanol permeability through polymeric, composite and a commercial Nafion 117 membranes as a function of the temperature. The methanol permeation through Nafion 117 is one order of magnitude higher compared to polymeric membrane with DS = 0.2, and about three times higher compared to that with DS = 0.8. As for other polymers belonging to the class of polyetherketones, the lower methanol permeability of SPEEK-WC in comparison with that of Nafion may be ascribed to a different membrane microstructure [12,14]. The Nafion microstructure combines the high hydrophobicity of the perfluorinated backbone with the extremely high hydrophilicity of the sulfonic acid functional groups. In the presence of water the sulfonic acid groups aggregate in hydrophilic clusters, which form water wide channels with a good connectivity. Both proton and water, but also polar molecule such as methanol, can easily

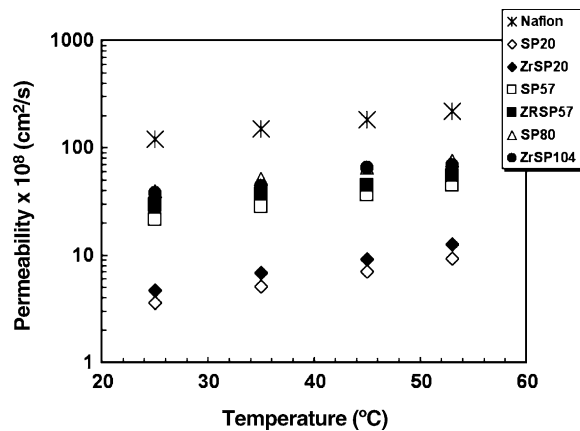Fig. 9. Pure MeOH uptake as a function of temperature.

Fig. 10. Methanol permeability of the polymeric and composite membranes based on SPEEK-WC polymer as a function of both DS of the polymer and of the temperature. For a comparison the permeability values measured in the same conditions for a commercial Nafion 117 membrane were also reported.
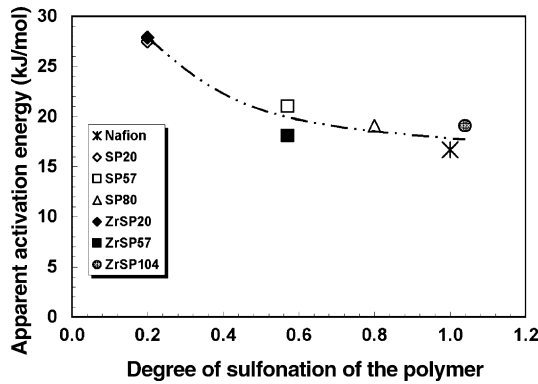
Fig. 11. Apparent activation energy for methanol permeation as a function of DS of the polymer. For Nafion 117 we have indicated arbitrary DS = 1.
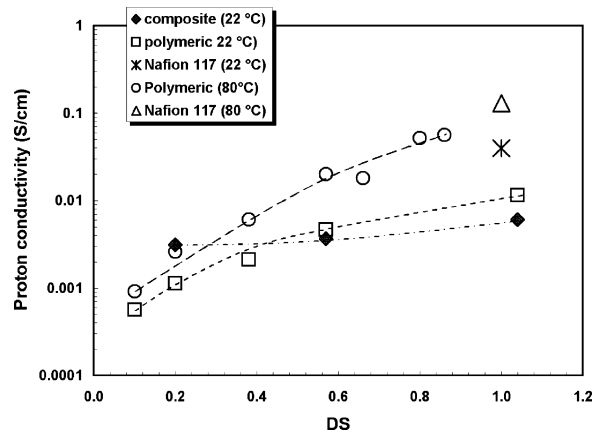

Fig. 12. Proton conductivity at 22 and 80 °C and 100% of relative humidity for both composite and polymeric membranes as a function of DS. The Nafion conductivity has been reported for a comparison.

permeate through these channels. As far as polyetherketones are concerned, the polyaromatic backbone is less hydrophobic due to the presence of oxygen atoms and carbonyl groups and less flexible than the polyaliphatic backbone of Nafion. This leads to a microstructure with narrow, dead end, and highly branched channels that is responsible for the lower methanol crossover in comparison with Nafion. On the other hand, an increase in DS results in a better connectivity between the hydrophilic clusters and therefore in enhanced methanol permeability as shown by Fig. 10. This trend is in agreement with literature data relative to similar systems based on sulfonated PEEK membranes [26,27]. The methanol permeability through the composite membranes is slightly higher (about 30%) with respect to the corresponding polymeric membranes at the same DS. Also, in the literature it has been reported than methanol permeability through similar composite membranes (SPEEK/ZrPh/PBI) was higher with respect to that of the corresponding polymeric ones [5].

The relation between methanol permeability and temperature can be described by the Arrhenius equation. From the slope of the Arrhenius curves, the apparent activation energy for methanol transport across the membranes can be calculated. The apparent activation energy and the permeation values for methanol transport are reported in Table 2. Fig. 11 shows the apparent activation energy for methanol transport through both the polymeric and composite membranes as a function of the degree of sulfonation of the polymer. An apparent activation energy of $16.7\,\mathrm{kJ\,mol^{-1}}$ has been measured for Nafion, in good agreement with literature data: $18\,\mathrm{kJ\,mol^{-1}}$ [22], $12\,\mathrm{kJ\,mol^{-1}}$ [26] and $10\,\mathrm{kJ\,mol^{-1}}$ [18]. For SPEEK-WC membranes, the appar-

ent activation energy decreases increasing the DS, being by only $3–4\,\mathrm{kJ\,mol^{-1}}$ greater than that of Nafion 117 membrane for DS higher than 0.57. A similar dependence of activation energy on DS was also exhibited by SPEEK membranes with DS of 0.39 and 0.47, although higher activation energy values (41 and $33.5\,\mathrm{kJ\,mol^{-1}}$, respectively) were reported [12]. For composite membranes, the apparent activation energy is close to that of the corresponding polymeric membranes. This seems to indicate that the filler does not alter to a significant extent the polymer microstructure and that the methanol diffusion occurs mainly through the hydrophilic clusters of the polymeric matrix.

3.5. Proton conductivity

The proton conductivities (σ) of both the SPEEK-WC with DS from 0.10 to 1.04 and Zr(SPP)/SPEEK-WC composite membranes were measured at room temperature and at 80 °C with 100% relative humidity. Prior to measurements, all membrane samples were soaked in water for at least 10 h for a full hydration. A Nafion 117 membrane sample was also measured in the same conditions. At 22 °C and 100% RH, the Nafion conductivity resulted $3 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$. This value is in good agreement with those reported in literature: $1.78 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ [28], $3 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ [19] and $5 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$, measured in water vapour at 20 °C and 100% RH [29], $6.8 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$, measured in water vapour at 30 °C and 100% RH [30]. Fig. 12 compares the proton conductivity of SPEEK-WC, composite

Table 2
Methanol permeability through polymeric, composite and a commercial Nafion 117 membranes, at various temperatures and apparent activation energy

Membrane	$T = 25\,°C$, $P \times 10^8$ ($\mathrm{cm^2\,s^{-1}}$)	$T = 35\,°C$, $P \times 10^8$ ($\mathrm{cm^2\,s^{-1}}$)	$T = 45\,°C$, $P \times 10^8$ ($\mathrm{cm^2\,s^{-1}}$)	$T = 53\,°C$, $P \times 10^8$ ($\mathrm{cm^2\,s^{-1}}$)	E_a ($\mathrm{kJ\,mol^{-1}}$)
Nafion 117	120	150	183	220	16.7
ZrSP20	4.7	6.8	9.2	12.6	27.9
ZrSP57	29	37	45	55	18.1
ZrSP104	38	44	65	69	19.1
SP20	3.6	5.1	7.0	9.3	27.5
SP57	21.5	28.1	36.5	44.6	21.0
SP80	39.5	51.6	65.1	76.1	19.1

and Nafion membranes as a function of DS. At 22 °C the proton conductivity of the SPEEK-WC membranes changes from 5.6×10^{-4} S cm^{-1} for DS = 0.1 to about 1×10^{-2} S cm^{-1} for DS = 1.04. The proton conductivities of the SPEEK-WC membranes measured in this work were slightly higher than those reported by Kaliaguine et al. [10] for SPEEK membranes prepared using DMF as a solvent and carrying out the measurements in very similar operative conditions. They reported at 25 °C $\sigma \approx 0.9$–2.5×10^{-3} S cm^{-1} for SPEEK with DS 0.58–0.59, while a value of $\sigma \approx 4.6 \times 10^{-3}$ S cm^{-1} for SP57 membrane with DS 0.57 has been measured in this work. At 80 °C and 100% RH, the proton conductivity as a function of the DS of the polymer obviously is higher than that at 22 °C, but it shows the same trend. Probably, the differences are due not only to temperature but also to the water uptake which is expected to increase with temperature. Also in this case, conductivity values obtained in this work were comparable to those reported by Vetter et al. [13] for SPEEK and similarly SPEKK membranes. At 80 °C and 100% RH, for SPEEK (DS 0.48) and SPEKK (DS 0.48) they indicated $\sigma \approx 2.4 \times 10^{-2}$ and 1.6×10^{-2} S cm^{-1}, respectively. In similar conditions a value of $\sigma \approx 2 \times 10^{-2}$ S cm^{-1} for SP57 membrane has been measured. Then, the proton conductivity values of sulfonated poly(etherketone)s are similar to those of SPEEK-WC measured in the same conditions. The proton conductivity, at 22 °C and 100% RH, of the composite membranes increases of about two times with increase in the polymer DS from 0.2 to 1.04. The conductivity of the composite membrane with DS 0.2 was three times higher than that of the polymeric membrane, but for DS 1.04 the same conductivity ratio was about 0.5. Therefore, the introduction of Zr(SPP) into SPEEK-WC improves the proton conductivity only for low DS values. A similar trend was confirmed for Nafion/ZrSPP composite membranes at low temperatures [31].

The proton conductivity (σ) and methanol permeability (P) are two very important parameters to characterize the membranes in view of their use in a DMFC. The membrane selectivity (α) can be expressed as the σ/P ratio [18]:

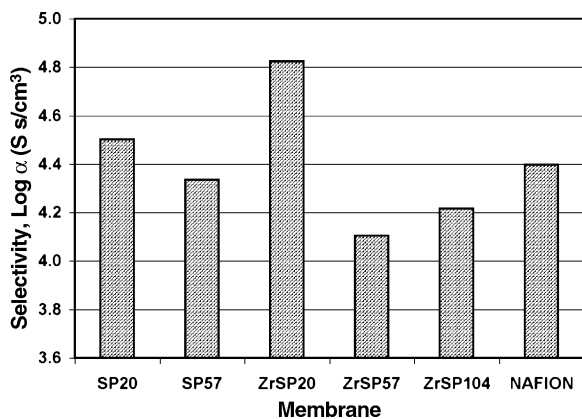$$\alpha = \left(\frac{\sigma}{P} \right) \qquad (4)$$

Fig. 13. A comparison of the log selectivity (conductivity/methanol permeability) (at 25 °C) among polymeric and composite membranes with various DS and a Nafion membrane.

Generally, in literature the logarithm of α, defined as $\beta = \log \alpha$, is reported.

A good membrane to be used in a DMFC must have both a high conductivity and a low methanol permeability and, therefore, a high α or β value. Fig. 13 shows the β values for polymeric and composite SPEEK-WC membranes, as well as for a Nafion 117 membrane. The selectivity of ZrSP20 composite membrane was more than two times that of Nafion 117, while the selectivity of pure SP20 membrane was about 27% higher than that of the Nafion.

4. Conclusions

Sulfonated poly(etheretherketone)s with a card group (SPEEK-WC) and with a wide range of DS were prepared. Also, Zr(SPP)/SPEEK-WC composite membranes obtained incorporating an amorphous zirconium phosphate sulfophenylenphosphonate gel with a fixed 20 wt% Zr(SPP) were prepared and characterized. Water and methanol uptake, mechanical properties, methanol permeability and proton conductivity were measured. Composite membranes absorb less water and methanol than the polymeric ones. Besides, water and methanol absorption does not increase significantly with temperature on the contrary of the polymeric membranes, especially in the case of high DS. Young's modulus of all composite and polymeric membranes were higher than that of Nafion 117 membrane. However, the elongation at break percentage, and therefore plasticity, was higher for Nafion than that of the SPEEK-WC based membranes. The composite membranes were less elastic and more brittle with respect to the polymeric ones. Methanol permeability through composite membranes was higher (about 30%) than that of the corresponding polymeric membranes. Methanol permeability of both polymeric and composite membranes was lower than that of Nafion 117 membrane. The apparent activation energy for methanol permeation decreases increasing DS, but there are no relevant differences between the composite and polymeric membranes. The apparent activation energy for membranes with high DS was close to that of Nafion. The proton conductivity increases with DS. However, for composite membranes the increase is not significant. The proton conductivity reflects the increase of water uptake with DS and temperature. At room temperature, the proton conductivity of the SPEEK-WC membrane with high DS (1.04) was about three to four times lower that of Nafion. However, interesting results were obtained considering the selectivity, here express as proton conductivity/methanol permeability ratio. This is an important parameter to characterize membranes to use in a DMFC. At 25 °C, the more interesting membranes are that with a low DS because they have a higher selectivity with respect to Nafion membrane.

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