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Keywords	*PEEK-PES copolymers; chlorosulfonic acid; Copolymer electrolyte membranes; impedance spectroscopy; PEMFC*
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Corresponding Author	*Belén Levenfeld*
Corresponding Author's Institution	*Universidad Carlos III de Madrid*
Order of Authors	*Belén Levenfeld, Ana M Martos, Miriam Biasizzo, Francesco Trotta, Carmen del Rio, Alejandro Varez*
Suggested reviewers	*Hansong Cheng, Juana Benavente, Tae-Hyun Kim, Enrico Drioli, Cristina Iojoiu*

Synthesis and characterization of sulfonated PEEK-WC-PES copolymers for fuel cell proton exchange membrane application.

A.M.Martos[a], M.Biasizzo[b], F.Trotta[b], C. del Río[c], A.Várez[a], B.Levenfeld[a]*

[a] Universidad Carlos III de Madrid, Department of Materials Science and Engineering and Chemical Engineering, Avda. Universidad, 30. 28911 Leganés, Madrid, Spain

[b] Department of Chemistry. Università degli Studi di Torino, 10125 Torino, Italy

[c] Institute of Polymer Science and Technology (CSIC), C/Juan de la Cierva 3, 28006 Madrid, Spain

*Corresponding author. Tel: 0034 916249915; fax: 0034 916249430.

E-mail address: *bll@ing.uc3m.es (B. Levenfeld)

Abstract

In this work we have developed new sulfonated cardo *(lactonic group)* PEEK-WC-PES random copolymers with different molar ratio. The degree of sulfonation was determined from elemental analysis and ion-exchange capacity (IEC). Sulfonation levels from 0.64 to 1 were easily achieved by varying and controlling the reaction conditions. Proton conductivity was evaluated by impedance spectroscopy (EIS). Activation energy for proton transport, determined by conductivity measurements ranged between 11 and 15 kJmol^{-1}, suggesting a vehicular proton transport mechanism. The membrane with better performance in single fuel cell was PEEK-SWC-PES 70:30 with maximum power and current densities of 93.6 mWcm^{-2} and 340 mAcm^{-2}, respectively.

Keywords: PEEK-PES copolymers; chlorosulfonic acid; Copolymer electrolyte membranes; impedance spectroscopy; PEMFC

1 Introduction

During the last years, the use of fuel cells has been growing exponentially. Among all different types of fuel cells, the proton exchange membrane fuel cell (PEMFC) is one of

the most promising. This mainly responds to its high efficiency, adaptable size and low operating temperature [1]. Nafion is the membrane most frequently used given its several advantages, including excellent mechanical properties, good chemical and electrochemical stability and high acidity from SO_3H groups. Nevertheless, it also presents some drawbacks, such as low conductivity above 100°C, high cost [2], low conductivity at reduced relative humidity and high methanol crossover [3]. Therefore, many efforts are undergoing in order to replace Nafion with other polymers with lower cost and not so dependent on humidity [4]. Sulfonated aromatic hydrocarbon polymers have been proposed as a good alternative to replace perfluorosulfonic acid membranes [4-7]. Such polymers are sulfonated polyimides [8], polyether etherketones (PEEK) [9-12], polysulfones and polyether sulfones (PES) [13-15].

Sulfonated copolymers based on PEEK and PES (PEEK-PES) [13,16-17] have been extensively studied as a good alternative to Nafion because of their good mechanical, thermal and chemical properties. They can be obtained by blending the homopolymers or by copolymerization of the corresponding monomers. W. Junzuo. *et al.* [16] synthesized block copolymers PEEK-PES from oligomers by aromatic nucleophilic substitution. In their research, they found that the two polymers form a compatible copolymer, which may have a high fuel cell performance given its high thermal stability. M. Guo *et al.* [17] synthesized block copolymers PEEK-PES from oligomers, which were synthesized through the monomers. However, such copolymers lacked of purity, since one of the repeat PEEK oligomer unit had the substituent methoxyphenyl group (OCH_3-C_6H_4) in p- or m- positions. Once the copolymer was obtained, the sulfonation reaction with H_2SO_4 occurred in the methoxyphenyl group. In this study, the most interesting results found include the conductivity obtained at 80ºC ($2.1 \cdot 10^{-1}$ Scm^{-1}) and the good mechanical and thermal properties exhibited. Regarding the blending approach, H-L. Wu *et al.* [18] firstly sulfonated PEEK commercial polymer with H_2SO_4 (>95%) and then prepared different blends with PES commercial polymer. The study concluded that the conductivity did not show a linear behaviour with the amount of PEEK. Room temperature conductivity for this blend was found to be $3.4 \cdot 10^{-2}$ Scm^{-1}, while for Nafion 117 (measured under the same conditions) it was $8 \cdot 10^{-2}$ Scm^{-1}.

Polyether etherketone with *cardo (lactone)* groups (PEEK-WC) is an amorphous polymer with high thermal and mechanical resistance as main characteristics and it is soluble in different organic solvents such as DMF, DMSO, DMAc or THF [12]. On the other hand, polyether sulfone with *cardo* groups (PES-WC) is a new kind of thermoplastic–engineering material with high mechanical properties and good thermal and chemical resistance. Moreover, the presence of the *cardo* group on the PES backbone contributes to reduce its crystallinity [19]. According to this, sulfonated

PEEK-WC-PES copolymers are envisioned as good candidates for polymer fuel cell electrolytes despite their undesirable water uptake, which punishes mechanical properties in wet stage. There are not many papers in the literature regarding these copolymers. Y. Li *et al.* [20] prepared blends with sulfonated PEEK and sulfonated PES-WC at different molar ratios. The PES polymer with WC group (*cardo* group) made the blend compatible. Additionally, the structure and organization of the hydrophilic domains showed no significant differences at different molar ratios. The conductivity value of SPEEK40-SPESWC60 was found to be $9 \cdot 10^{-2}$ Scm^{-1} at 60ºC.

In this context, the purpose of this work was the preparation and characterization of novel random copolymers PEEK-WC-PES membranes. The copolymers were synthetized by copolymerization of monomers: 4,4'-Difluorobenzophenone (DBP) and Bis (4-fluorophenyl) sulfone (BPS) at different molar ratios. In addition, a phenolphthalein monomer was used as linker, which has a bulky group called *cardo (lactone)* (WC). Once the copolymers were characterized, the sulfonation reaction was performed using chlorosulfonic acid (ClSO$_3$H) as sulfonating reagent. PEEK-WC-PES and sulfonated copolymers (PEEK-SWC-PES) membranes were characterized by ^{1}H-NMR for structural analysis, elemental analysis (EA) and ion exchange capacity (IEC) for the degree of sulfonation. In addition, water uptake study and thermal analysis (thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)) were performed. Membrane conductivity was determined from impedance spectroscopy (EIS) measurements, which were carried out with the membranes in contact with HCl solutions at different concentrations. The study of the conductivity at different temperatures permitted to obtain the activation energy associated to the ion transport in the membrane and to determine the main mechanism involved in the diffusion process. Finally, the membranes were characterized into a single cell in order to determine cell performance at 50ºC and 100%RH.

2.- Experimental

2.1.- Materials

Phenolphthalein (phph), 4,4'-Difluorobenzophenone (DBP) and Bis (4-fluorophenyl) sulfone (BPS), were crystallized by ethanol before used. Potassium carbonate (K$_2$CO$_3$) was dried in an oven at 120ºC overnight. All reagents were milled and lyophilized before used. Chlorosulfonic acid (ClSO$_3$H, 98%), N,N-dimethylacetamide (CH$_3$C(O)N(CH$_3$)$_2$, DMAc), Toluene (C$_7$H$_8$) and DMSO-d$_6$ were supplied by Sigma-Aldrich. Toluene and DMAc were dried before used.

2.2.- Synthesis of PEEK-WC-PES Copolymers

The copolymerization reaction was performed according to the procedure described by J. Pang et al. [21]. In a three-neck round bottom flask provided with a Dean-Stark trap with a reflux condenser, through which 47 ml of anhydrous DMAc and 40 ml of toluene were added. Subsequently, 3.25 g (2.35 10^{-2} mol) of anhydrous K_2CO_3, 5 g (1.57 10^{-2} mol) of phenolphthalein, 3.58 to 0.399 g (1.41 10^{-2} – 1.57 10^{-3} mol) of BPS and an amount of DBP from 0.34 to 3.08 g (1.57 10^{-3} - 1.4 10^{-2} mol) as a function of the molar ratio desired, for the different molar ratio synthesized, was slowly added under vigorous stirring. The nominal molar ratio of the copolymers prepared is shown in Table 1. The amount of phenolphthalein was always de same so its molar fraction in all the copolymers was 0.5.

The reagents were heated for 2 hours at 145 ºC in order to favour the azeotropic water elimination. Subsequently, temperature was risen until 165 ºC for further 4 hours. Once the reaction was over, the solution was cooled at room temperature to favour precipitation of the polymer in an excess of ethanol. After 24 hours, the synthesized copolymers were filtered, washed with ethanol and dried at room temperature under vacuum. The same procedure was applied to obtain PEEK/PES copolymers with different molar ratios. The structure of the copolymers may be a statistic mixture of any possible sequences (DBP-Ph-DBP, DBP-PH-BPS, and BPS-PH-BPS) (Fig.1).

2.3.- Sulfonation of PEEK-WC-PES copolymers

The sulfonation reaction was carried out according to the procedure described by Trotta et al with minor modification [22]. Briefly, in a neck round bottom flask 40 ml of ClSO₃H, 2 g of copolymer PEEK-WC-PES was slowly added under vigorous stirring at 35°C (Fig.1). The mixture was allowed to react for 30 minutes. Once the reaction was over, the sulfonated copolymer was precipitated in an ice bath to eliminate the excess of ClSO₃H. Then, the sulfonated copolymer (PEEK-SWC-PES) was filtered and washed several times with deionized water up to neutrality and dried at room temperature.

2.4.-Membrane preparation

The non-sulfonated and sulfonated copolymers were dissolved (5 wt%) in DMAc. The polymeric solutions were cast on Petri glass dishes. Afterward, the cast membranes were dried in an oven at 60ºC for 48 h. The membranes were immersed in water to eliminate possible traces of solvent and, then, dried at room temperature. The thickness of membranes was in the 100-200 µm range.

2.5.- Membrane characterization

2.5.1 NMR analysis

Liquid ^{1}H NMR spectra of all samples were recorded on a spectrometer Bruker Avance DPX 300 MHz using dimethylsulfoxide (DMSO-d$_6$) as solvent. The tetramethylsilane (TMS) was used as internal reference.

2.5.2 Elemental analysis

Elemental analysis of copolymers based on sulfur to carbon ratio determinations was performed by using a manual FlashEA elemental analyzer. C, H and S were converted to CO_2, H_2O, SO_2 at 900ºC in a column containing an oxidant agent. They were separated in a GC column containing molecular sieves and detected by a thermal conductivity detector (TCD). The percentages of C, H and S were determined after elaborating the respective calibration curves with different standards. For each composition, three analyses were performed.

2.5.3 Ion-exchange capacity

The ion-exchange capacity values of the membranes were determined using an automatic titrator (916 Ti-Touch, Metrohm). Membrane samples (1 g) in acid form (after exchange in 1M HCl solution for at least 24h) were immersed in 2M NaCl solution for 24h to liberate the H$^+$ ions. The resulting solutions were titrated with normalized 0.01M NaOH. The IEC values were calculated with the equation (1):

$$IEC(equiv/g) = \frac{V_{NaOH} x [NaOH]}{W_{dry}}$$

(1)

Where V$_{NAOH}$ is the volume of NaOH consumed, [NaOH] is the concentration of NaOH and W$_{dry}$ is the weight of the membrane in dry state.

2.5.4 Thermal analysis

Thermal characterization of copolymers was performed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA experiments were carried out with a Perkin Elmer Pyris TGA1. The analyses were performed under nitrogen atmosphere, from 50 to 700ºC at a heating rate of 10ºCmin^{-1}. DSC measurements were performed, under nitrogen atmosphere, with a Perkin Elmer Diamond calorimeter. The samples were heated from 50 to 300 °C at a heating rate of 10°Cmin^{-1}, maintained 5 minutes at both temperatures and then cooled to room temperature at 20°Cmin^{-1}. Subsequently, samples were heated once more at the same conditions. The midpoint

of the enthalpy increment, in the transition region of the second heating, was used to determine the Tg.

2.5.5 Water uptake and swelling degree

Water uptake (WU) of all membranes was determined at room temperature. Samples were immersed for 72h in deionized water. After quickly cleaning off the water excess from the surface with a paper, all samples were weighted. After drying, in an oven at 60ºC for 24h, the samples were weighted again in order to determine their mass in dry state.

Water uptake (WU) was calculated using the equation (2):

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} x100 \tag{2}$$

Swelling degree (SD) was calculated by the equation (3):

$$SD(\%) = \frac{t_{wet} - t_{dry}}{t_{dry}} x100 \tag{3}$$

where, W_{wet} and W_{dry} are the weights of the membranes in wet and dry state and t_{wet} and t_{dry} are the thickness of the membranes in wet and dry state, respectively.

2.5.6 Mechanical measurements

The mechanical properties of the wet membranes were determined at room temperature by uniaxial tensile tests. For this purpose, 5 mm × 25 mm samples were tested to failure at a crosshead speed of 0.5 mmmin^{-1} in a Universal Testing Machine (Shimadzu model Ag-1) with an operating load cell of 1 kN. The number of samples tested for each membrane was at least three. Prior to mechanical testing, the sample was immersed in distilled water at 50 °C for 3 h.

2.5.7 Impedance spectroscopy

Impedance spectroscopy measurements (EIS) were carried out in a liquid test cell similar to that described elsewhere [23] and using an impedance analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287). The cell has two

compartments, the membrane was tightly clamped between two half cells by o-rings. An Ag/AgCl reference electrode was used to measure the electrical potential difference between both half-cells and two graphite electrodes are used for current probes AC impedance spectra of the membranes were recorded in the 10^{-1}-10^{6} Hz frequency range by applying a voltage with an amplitude of 10mV. Conductivity values were determined for six different HCl solutions ($10^{-3} \leq c \leq 0.1M$), at room temperature. The solutions on both sides of the membrane had the same concentrations. Before the measurement, the membranes were stabilized in a $10^{-3}M$ HCl solution during 24h.

The proton conductivity (σ in Scm^{-1}) is given by the following equation:

$$\sigma = \frac{l}{R \times A} \tag{4}$$

where l is the thickness of the membrane (cm), R is resistance (Ohm) and A is the area of the membranes (cm^2).

Measurements at different temperatures (30-80°C) were performed in the same conditions and using a temperature chamber KMF 115 (Binder GmbH). To ensure the repeatability of the measurements, at each temperature and before running the measurement, a dwell time of 15 minutes was defined. This time was enough for the system to reach a stable temperature because changes in conductivity less than 0.1% were observed after repeated measurements.

The activation energy (Ea in $KJmol^{-1}$) was calculated using the following equation:

$$\ln \sigma = \ln A - \frac{E_a}{RT} \tag{5}$$

where σ, A, R and T are, respectively, the proton conductivity in Scm^{-1}, the pre-exponential factor, the ideal gas constant in $Jmol^{-1} K^{-1}$, and the temperature in K.

2.5.8 Fuel Cell Performance.

Performance tests of the MEAs have been carried out using a Scribner 850e multi range fuel cell test system using H_2 as fuel and O_2 as oxidant (200 $mLmin^{-1}$). The tests were run at atmospheric pressure, 50°C cell temperature and 100%RH. Prior to record the polarization curve, cells were activated at a constant current until stable performance was achieved at every experimental condition.

2.5.9 In situ through-plane proton conductivity of the membranes.

The through-plane proton conductivity of the copolymer membranes has been determined on the MEAs at 50ºC, 100% RH by means of electrochemical impedance spectroscopy (EIS) using a potentiostat Autolab PGStat30 equipped with a FRA module. Commercial Nafion 112, Nafion 115 and Nafion 117 membranes, used as reference materials, were tested at 60ºC, 100%RH. The cell was continuously supplied (200 mLmin^{-1}) with humidified H_2 (SHE, anode) and N_2 (cathode). The amplitude of the sinusoidal signal was 10 mV and the frequency range 104 Hz to 1 Hz. The spectra were recorded under a DC bias potential of 0.45 V. The through-plane proton conductivity (σ) was obtained using the equation (4), where, in this case A is the active area of the MEA (5 cm^2), I is the membrane thickness (cm) and R is resistance (Ohm), which was measured at the frequency that produced the minimum imaginary response. Each sample was measured five times after achieving a constant value to ensure good data reproducibility.

3.- Results and discussion

3.1. Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

The chemical structure of copolymers was analyzed by ^{1}H-NMR spectroscopy.
The ^{1}H-NMR spectra of non-sulfonated and sulfonated copolymers are reported in Figure 2. In the PEEK-WC-PES spectra (Figure.2.a), the intensity of H1 and H2 peaks are increased with the molar ratio of the DBP monomer, causing the intensity of H7 and H8 (BPS peaks) to decrease.

In case of PEEK-SWC-PES (Figure 2.b), a new peak appeared at 8.12 ppm, which corresponds to the proton adjacent to the sulfonic group (H4") [18, 24]. The theoretical calculations demonstrated that the sulfonic group is bonded to the aromatic ring adjacent to the ether group in the phenolphthalein monomer. The sulfonation reaction happened at the same position in the three possible copolymers.

3.2. Elemental analysis

The composition of each copolymer was determined by C, H and S elemental analysis. The experimental molar ratio was determined from the S/C ratio. The percentages of C, H and S and the nominal and experimental compositions of PEEK-WC-PES copolymers are reported in Table 1. Three analyses per each composition were performed and in the table average value and the standard deviation is indicated.

Table 1. Elemental analysis (including standard deviation), nominal and experimental molar ratio for PEEK-WC-PES.

Copolymer	%C	%H	%S	Nominal molar ratio	Experimental molar ratio
PEEK-WC-PES 10:90	69.81±0.39	3.69±0.04	5.16±0.05	10:90	11:89
PEEK-WC-PES 20:80	68.63±0.35	3.63±0.02	4.43±0.06	20:80	22:78
PEEK-WC-PES 30:70	68.60±0.37	3.63±0.03	3.84±0.04	30:70	32:68
PEEK-WC-PES 40:60	68.38±0.34	3.60±0.03	3.28±0.05	40:60	42:58
PEEK-WC-PES 50:50	57.28±0.32	3.04±0.01	2.37±0.03	50:50	50:50
PEEK-WC-PES 60:40	63.55±0.33	3.27±0.02	1.81±0.02	60:40	65:35
PEEK-WC-PES 70:30	62.36±0.33	3.30±0.03	1.34±0.01	70:30	74:26
PEEK-WC-PES 80:20	65.12±0.34	3.38±0.04	0.89±0.01	80:20	83:17
PEEK-WC-PES 90:10	72.26±0.40	3.72±0.05	0.41±0.01	90:10	93:7

The content of S in the copolymers decreased as the ketonic structural unit increased in agreement with the nominal molar ratio. As it can be seen in Table 1, the experimental compositions obtained are very close to the nominal ones. The experimental molar ratio of sulfonic structural units in the copolymer is lower than the nominal one. This fact could indicate that the reactivity of BPS was higher than that of DBP, such low composition of the sulfonic structural unit may be related to the oligomers formation or to the presence of cycles [25].

The percentages of C, H, N and S obtained for sulfonated copolymers and the degree of sulfonation (DS_{EA}) are shown in Table 2. The sulfonation degrees were determined from the elemental analysis results taking into account the experimental molar ratio of the copolymers determined previously.

The content of S in the sulfonated copolymers increased as the structural sulfonic unit increased, which is in agreement with the nominal molar ratio.

The degree of sulfonation of all copolymers was quite similar, since the sulfonation reaction occurs only in the phenolphthalein monomer as it was incorporated in a constant molar ratio. The degree of sulfonation was approximately one sulfonic group per monomeric unit [26]. Moreover, we observed that the percent of S decreased with the amount of ketonic structural unit, as a consequence of the absence of S in the PEEK repeat unit.

Table 2. Elemental analysis (including standard deviation), DS_{EA}, Ion-exchange capacity and DS_{IEC} for PEEK-SWC-PES.

Copolymer	%C	%H	%S	DS_EA	IEC	DS_IEC
PEEK-SWC-PES 10:90	59.54±0.32	3.27±0.04	8.06±0.08	0.74	0.93	0.53
PEEK-SWC-PES 20:80	56.85±0.29	3.29±0.03	8.07±0.06	0.94	1.15	0.66
PEEK-SWC-PES 30:70	55.92±0.30	3.13±0.04	7.83±0.07	1.00	1.18	0.68
PEEK-SWC-PES 40:60	60.11±0.35	3.25±0.05	7.24±0.05	0.88	1.11	0.63
PEEK-SWC-PES 50:50	60.31±0.34	3.42±0.02	6.47±0.04	0.81	1.14	0.64
PEEK-SWC-PES 60:40	60.81±0.32	3.55±0.03	5.58±0.04	0.77	1.05	0.58
PEEK-SWC-PES 70:30	60.36±0.34	3.37±0.05	5.56±0.05	0.87	1.20	0.67
PEEK-SWC-PES 80:20	64.25±0.33	3.56±0.06	4.66±0.03	0.72	0.96	0.52
PEEK-SWC-PES 90:10	65.07±0.35	3.48±0.03	3.75±0.03	0.64	0.92	0.50

3.3. Ion-exchange capacity

The IEC values of the membranes were determined by classical titration. The DS of the studied membranes was calculated from the experimental IEC values using the following equation:

$$DS_{IEC} = \frac{IEC/1000}{(1 - \frac{IEC}{1000} x M_{SO_3H}) x \frac{1}{M_{copolymer}}} \quad (6)$$

Where, $M_{copolymer}$ is the weight of each membrane and $M_{SO3H} = 80$ gmol^{-1}. M_{SO3H} is the molecular weight of the $-SO_3H$ group.

IEC values and DS calculated from equation 6 are shown in Table 2.

Degree of sulfonation for the different copolymers calculated by both elemental analysis and ion exchange capacity are compared in Figure 3.

The results show that DS values obtained by both techniques present similar trends with the %molar of PEEK, but in all the cases, DS values obtained by EA were higher than those obtained by IEC. This fact may be due to an incomplete Na+/H+ exchange related to the possible inaccessibility of some sulfonic acid groups embedded in the bulk of the ionomer. The presence of some Na, at least in the membrane surface, was confirmed by EDS analysis.

3.4. Thermal analysis

The thermal stability of PEEK-WC-PES and PEEK-SWC-PES copolymers was studied by TGA (Figure 4). TGA curves of PEEK-WC-PES copolymers present two weight losses: between 50 and 200ºC, which correspond to absorbed water. The last weight loss, above 375ºC, was attributed to the main chain polymer decomposition. In the case of sulfonated copolymers (PEEK-SWC-PES), three main weight losses are detected: (i) the mass loss at temperature ranging from 50 to 200ºC corresponds to the evaporation of absorbed water bonded to sulfonic groups, (ii) the weight loss between 200 and 350ºC was attributed to the desulfonation process, which involves release of SO_2 and SO gases and(iii) the third step, above 350ºC, was related to the main chain decomposition [18,24].

In both copolymer series (PEEK-WC-PES and PEEK-SWC-PES), the thermal stability increases with the content of ketonic structural units in the copolymer. After sulfonation, the thermal stability of the different copolymers slightly decreased up to 225ºC, where the desulfonation processes start. However, the thermal stability of PEEK-SWC-PES is adequate within a conceivable temperature range of PEMFC applications [16].

The Tg was influenced by the difference in monomer molar ratio. The data showed (Figure 5) an increase in Tg with the increment of PES units in the copolymers. This behavior can be attributed to the fact that Tg of PES-WC (271ºC) is higher than that of PEEK-WC (233ºC). The Tg of the different copolymers was calculated with Fox's equation (7) [18].

$$\frac{1}{Tg_{PEEK-WC-PES}} = \frac{W_{PEEK-WC}}{Tg_{PEEK-WC}} + \frac{W_{PES-WC}}{Tg_{PES-WC}} \tag{7}$$

Calculated and experimental Tg values were similar as shown in Figure 5

The influence of degree of sulfonation on the glass transition temperature, Tg, was also studied. The Tg values obtained for 10:90, 20.80 and 30:70 of sulfonated copolymers were 280, 203 and 274 ºC, respectively. This increment is due to both, the *cardo* and the sulfonic groups. The sulfonic function groups increase the stiffness due to the intermolecular interactions, which make difficult the internal rotation of high molecular chain segments [18,22,24,27,28].

3.5. Water uptake and swelling degree

The evolution of the water uptake and swelling degree at room temperature of the studied membranes with different molar ratio is shown in Figure 6. It can be seen that the amount of absorbed water is similar in all sulfonated copolymers membranes, with values around 30%. This occurs because the different copolymers have similar number of sulfonic groups. In general, the swelling degree increases with the amount of PEEK structural unit, ranging between 5 and 14%.

Li *et al*. [20] also observed in SPEEK/SPESc blends an increase of the water uptake with the amount of SPEEK as a consequence of the presence of sulfonic groups or active sites in SPEEK. The difference regarding our copolymers is that the sulfonic groups are located in the phenolphthalein repeat unit, which remains constant for the different analyzed copolymers.

3.6 Mechanical measurements

The tensile strength and elongation at break (%) of PEEK-SWC-PES copolymers are shown in Figure 7. At least three specimens were tested per each molar ratio. The tensile strength and elongation at break values are summarized in Table 3, and correspond to the average value and the standard deviation. A high dispersion of values for each composition is observed.

The results showed that the tensile strength and elongation at break slightly increase with the amount of PEEK structural unit. This fact could be due to the higher tensile strength of the PEEK polymer regarding PES (98 and 83 MPa, respectively) [12,19]. All the copolymers presented a higher strength than Nafion membrane. However, the elongation at break of Nafion is considerably higher. The values of elongation at break of these copolymers were too low, highlighting the fragile nature of these membranes.

After sulfonation, the tensile strength of copolymers decreased (Table 3) because of the hydrophilic character of sulfonic groups, which allow water to act as an external plasticizer [29]. Despite such a decrease in tensile strength, the values of sulfonated copolymers were slightly higher than those of Nafion.

The tensile strength reported by Li et al. [20] for the blends of SPEEK and SPESWC increased with the amount of SPEEK. The values ranged from 33 to 40 MPa for SPEEK20-SPESc80 and SPEEK80-SPESc20, respectively. Comparing these values with those of our copolymers and SPEEK-SPESc, the tensile strength was lower than that of blends.

The mechanical properties and water uptake were related, in such a way that the increase in the water uptake provoked a decrease in mechanical properties.

Table 3. Tensile strength (MPa) and elongation at break (%) of PEEK-WC-PES and PEEK-SWC-PES membranes.

Membrane	Non-Sulfonated		Sulfonated		
	Tensile strength (MPa)	Strain at break (%)	Tensile strength (MPa)	Elongation at break (%)	DS
Nafion[1]	18	190	-	-	-
PEEK-WC-PES 10:90	35±2	3.1±0.5	36±2	6±2	0.73
PEEK-WC-PES 20:80	32±11	3.8±0.3	22±11	6±8	0.91
PEEK-WC-PES 30:70	40±3	6±2	25±9	4±3	0.99
PEEK-WC-PES 40:60	43±12	7±1	25±6	9±3	0.86
PEEK-WC-PES 50:50	40±10	5±1	31±9	10±2	0.81
PEEK-WC-PES 60:40	40±10	6±1	25±6	5±1	0.72
PEEK-WC-PES 70:30	43±11	5±1	21±1	12±3	0.83

[1] Data taken from reference [27]

3.7. Impedance spectroscopy analysis

The study of the electric properties of the membranes was performed using impedance spectroscopy (EIS). Figure 8.a shows the Nyquist plot obtained for a membrane, as an example, at different HCl concentrations ($10^{-3} \leq c \leq 10^{-1}$M). The spectra of all membranes with different composition present two clear arcs. The semicircle (high frequency arc (HFA)) could be associated to the membrane capacitance (or constant phase element) of the membrane acting in parallel with its resistance. The low frequency arc (LFA) is clearly deformed and is associated to the diffusion of electroactive species [30]. In all cases, the high frequency semicircle does not intercept the origin of the plot, indicating the presence of a resistive element in series with the other two processes [31]. This resistive element should be related to the electrolyte

(Figure 8.a). The size of the HFA semicircle changes with the HCl concentration of the solution.

Impedance data were corrected for overall sample geometry and are therefore reported in units of ohm·cm. The conductivity values were obtained from the inverse of the real part of the impedance, which is determined by the intersection with the abscissa of the high frequency arc of Nyquist plots. As expected, the proton conductivity associated to the membrane increases with the [HCl] (Figure 8.b). This behavior has been also observed in poly (ether ether sulfone) [32] and is attributed to the concentration dependence on the electrolyte solution embedded in the membrane matrix. For that reason, these measurements were used to determine the proton transport mechanism occurring in these membranes, while the conductivity of the membranes was determined in situ on the MEAs. The other sulfonated copolymers exhibited a similar behavior (data not shown) and the conductivity values are quite similar to that of Nafion 117 membrane measured under these specific experimental conditions (Figure 8).

The Nyquist plots of all sulfonated copolymers for [HCl] = 10^{-2} M are displayed in Figure 9.a. The influence of different composition in PEEK-SWC-PES did not significantly change the impedance values. This behavior could be also observed in Figure 9.b, where conductivity values of all polymer composites are displayed.

As it is known, the proton transport in polymeric membranes occurs via two mechanisms: 1) Grotthuss mechanism, where the protons "jump" from one water molecule to the next via hydrogen bonding. This mechanism requires a larger thermal activation, with Ea ≈ 14-40 KJmol^{-1} [20], and 2) vehicular mechanism in which the protons diffuse in combination with water into a complex [33]. This mechanism is characterized by lower activation energy in comparison with Grotthuss mechanism. To analyze the proton transport mechanism in these copolymer membranes, we studied the conductivity as a function of temperature. The temperature dependence of the proton conductivity for the different PEEK-SWC-PES copolymers is shown in Figure 10. Conductivity varies with temperature according to Arrhenius-like equation (5).

The apparent activation energy values for the different membranes are gathered in Table 4. As it can be seen, the conductivity values were not significantly different among them but fairly similar to the one we obtained for commercial membranes of Nafion 117. This value, resembling that reported for the fully hydrated Nafion 117 (12 kJmol^{-1}) [34], indicates that the vehicular model is the main proton transport mechanism in all the membranes and, consequently, the addition of BPS did not significantly change the proton conduction mechanism.

Table 4. Activation energy values for PEEK-SWC-PES membranes.

Membrane	Ea (kJ mol^{-1})
Nafion 117	10.7 ± 0.4
PEEK-SWC-PES 10:90	14 ± 1
PEEK-SWC-PES 20:80	13 ± 1
PEEK-SWC-PES 30:70	13 ± 1
PEEK-SWC-PES 40:60	11 ± 1
PEEK-SWC-PES 50:50	13 ± 1
PEEK-SWC-PES 60:40	14 ± 1
PEEK-SWC-PES 70:30	15 ± 2

3.8 Fuel Cell Performance.

In a single cell test, the maximum current and power densities can be determined at a particular voltage and different experimental conditions such as cell temperature, relative humidity or pressure of the reagents. Polarization curves of PEEK-SWC-PES 30:70, 50:50 and 70:30 at 50ºC and 100%RH are presented in Figure 11.

The behavior of the three copolymer membranes tested at such experimental conditions seems very similar, all presenting ~~poor~~ discrete performances as compared with Nafion 117 (see inset of figure 11). The membrane with the best performance was PEEK-SWC-PES 70:30, leading a maximum power density close to 90 mWcm^{-2} (65 mWcm^{-2} for 50:50 and 25 mWcm^{-2} for 30:70). The maximum current densities of different copolymers were 90 mAcm^{-2} for 50:50, 190 mAcm^{-2} for 30:70 and 340 mAcm^{-2} for 70:30.

3.9 In situ through-plane proton conductivity of the membranes

Electrochemical characterization of membranes by using the liquid cell (ex-situ method) described in 2.5.7 section is a useful and simple electrochemical method to estimate, in a fast way, the proton conductivity of PEM membranes [35,36]. It has been used by other authors to determine electrochemical properties of polysulfones [37] and hybrid

organic–inorganic materials [38]; however and as it was mentioned before the ionic conductivity of all the prepared membranes determined by this method was quite similar and even similar to that of nafion used as reference. In order to understand the limited performance observed for the copolymers in the single cell, *in situ* through-plane proton conductivity of the membranes was determined by EIS on the MEAs under humidified gases (100% RH),at 50ºC and atmospheric pressure. These experimental conditions imitate the practical fuel cell operating conditions used for polarization curves obtaining; thereby it is possible to avoid the [HCl] concentration dependence on the electrolyte solution, as previously mentioned. Figure 12 compares the impedance spectra obtained for PEEK-SWC-PES 70:30 and 30:70 with commercial Nafion112, Nafion115 and Nafion117. The ionic resistances were measured at the frequency that produced the minimum imaginary response. As it can be observed, the ionic resistances of the copolymer membranes are much higher, namely almost one order of magnitude than Nafion112, resulting in lower ionic conductivities than that of commercial Nafion. Table 5 compiles the data of proton conductivity obtained.

Moreover, the composition of PEEK-SWC-PES copolymers has very little influence on membrane conductivity. As it was noted above, the degree of sulfonation of all copolymers (IEC values) was quite similar because the sulfonation reaction occurred only in the phenolphthalein unit, which was incorporated in a constant molar ratio. Therefore, the modest performances of these copolymer membranes in single cell must be related to both, the low proton conductivity as compared to Nafion and the reduced mechanical properties of these materials in the hydrated state.

Table 5. In situ through-plane proton conductivity of PEEK-SWC-PES 30:70, 70:30 (measured at 50ºC, 100% RH) and commercial Nafion 112, 115 and 117 (measured at 50ºC, 100% RH). The standard deviation of five measurements are also indicated.

Membrane	*Thickness (μm)*	*R (Ω)*	*σ (mS cm^{-1})*
PEEK-SWC-PES 30:70	73	0.120	12.17±0.09
PEEK-SWC-PES 70:30	53	0.120	8.83±0.04
Nafion 112	51	0.031	32.90±0.05
Nafion 115	127	0.050	50.80±0.06
Nafion 117	178	0.064	55.63±0.04

4.-Conclusions

PEEK-WC-PES copolymers with different molar ratio were prepared and successfully sulfonated with chlorosulfonic acid. The experimental composition of PEEK-WC-PES was confirmed by elemental analysis. ^{1}H-NMR, IEC and elemental analysis studies confirmed that the sulfonation reaction actually took place.

^{1}H-NMR studies revealed that the sulfonic group is placed at position 4", which is close to the *cardo* group. All copolymers showed high thermal stability in the temperature range studied. The DSC measurements showed an increase in glass transition temperature with the content of BPS. The introduction of bulky sulfonic and *cardo* group in the copolymer increased the glass transition temperature. The tensile strength and elongation at break increased with the amount of ketonic structural unit. Nevertheless, in the case of sulfonated copolymers, the tensile strength and elongation at break decreased due to the hydrophilic domains. There were no significant differences found among all sulfonated copolymers regarding water uptake.

The conductivity values for the different membranes carried out in a liquid test cell, were not significantly different among them. The proton transport mechanism remained the same for all sulfonated copolymers, which showed that all the copolymers have similar structures and organizations of the hydrophilic domains. The low activation energy values indicated that the proton transport mechanism is predominantly vehicular. Although the tensile strength is improved compared to that of the nafion, however, the elongation at break values are considerably lower. In situ through-plane proton conductivity of the membranes on the MEAs, were lower than that of commercial nafion membranes and the membrane with better performance in single fuel cell was PEEK-SWC-PES 70:30 with maximum power and current densities of 93.6 mWcm^{-2} and 340 mA cm^{-2}, respectively.

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Figure Captions

Figure 1. Synthesis and sulfonation reaction of copolymers PEEK-WC-PES and PEEK-SWC-PES.

Figure 2. ^{1}H-NMR spectra of **a)** PEEK-WC-PES and **b)** PEEK-SWC-PES.

Figure 3. Estimation of the DS by ion-exchange capacity and elemental analysis.

Figure 4. Thermogravimetric analysis of **a)** PEEK-WC-PES and **b)** PEEK-SWC-PES.

Figure 5. Experimental and nominal Tg, calculated by Fox equation.

Figure 6. Water uptake and swelling degree of sulfonated copolymers.

Figure 7. Mechanical properties of sulfonated copolymers in wet state.

Figure 8. a) Impedance plot for PEEK-SWC-PES 20:80 membrane with the HCl concentration and electrical equivalent circuit. **b)** Evolution of the ionic conductivity of PEEK-SWC-PES 60:40 and Nafion 117 with the HCl concentration.

Figure 9. a) Nyquist plot for all membranes in contact with a 10^{-2} M HCl solution and **b)** Proton conductivity at room temperature ([HCl] = 10^{-2} M) for the different membranes.

Figure 10. Evolution of the proton conductivity versus temperature (Arrhenius plot) for different membranes ([HCl] = 10^{-2} M). The estimated uncertainties of conductivity measurements were less than 1%

Figure 11. Polarization and power density curves of PEEK-SWC-PES 30:70, 50:50 and 70:30 at 50ºC and 100%RH. The Nafion membrane was showed as inset.

Figure 12. Impedance spectra of PEEK-SWC-PES 30:70, 70:30 and commercial Nafion 112, 115 and 117. In the inset the best electrical equivalent circuit obtained from the fitting of the experimental data is shown.
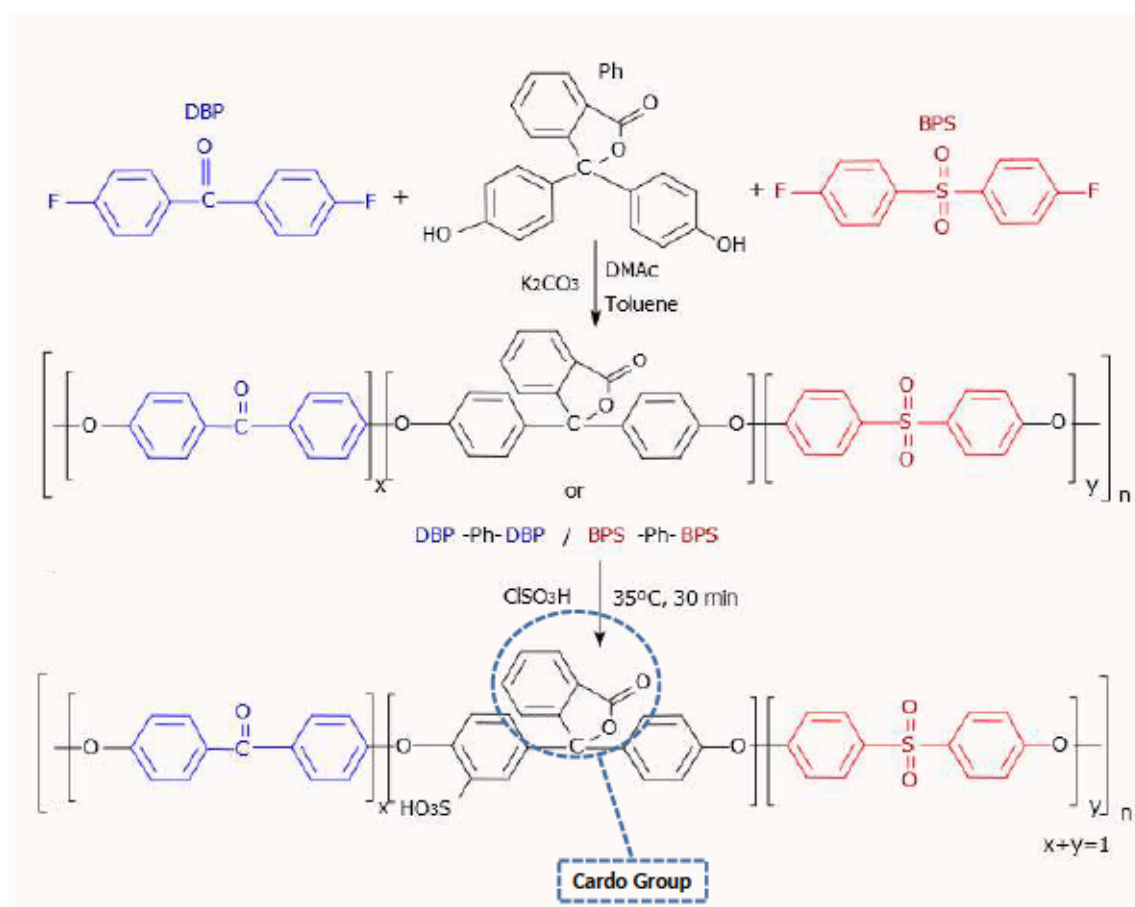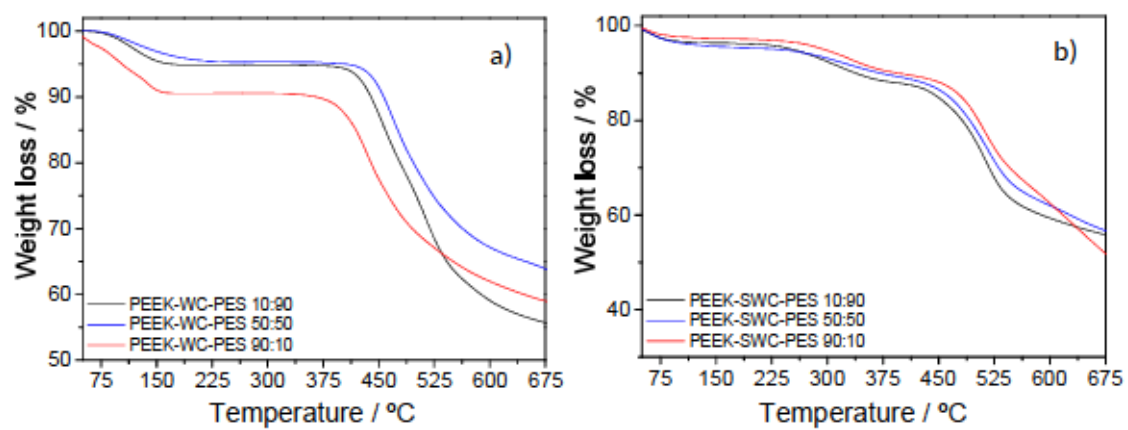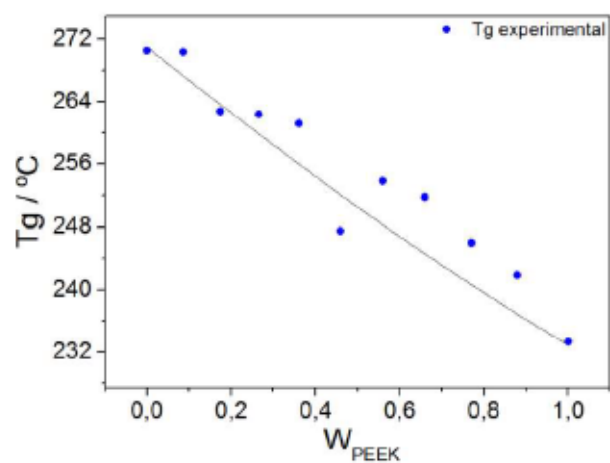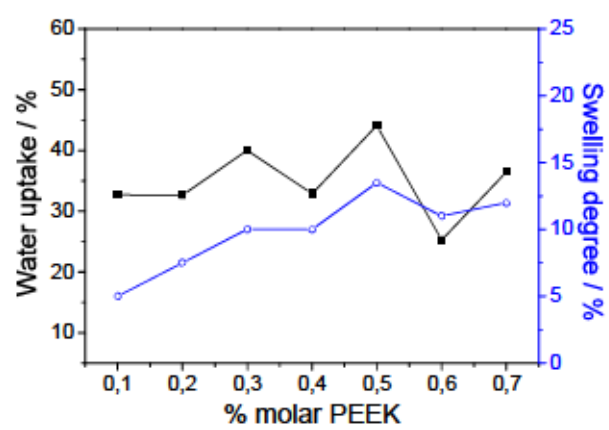
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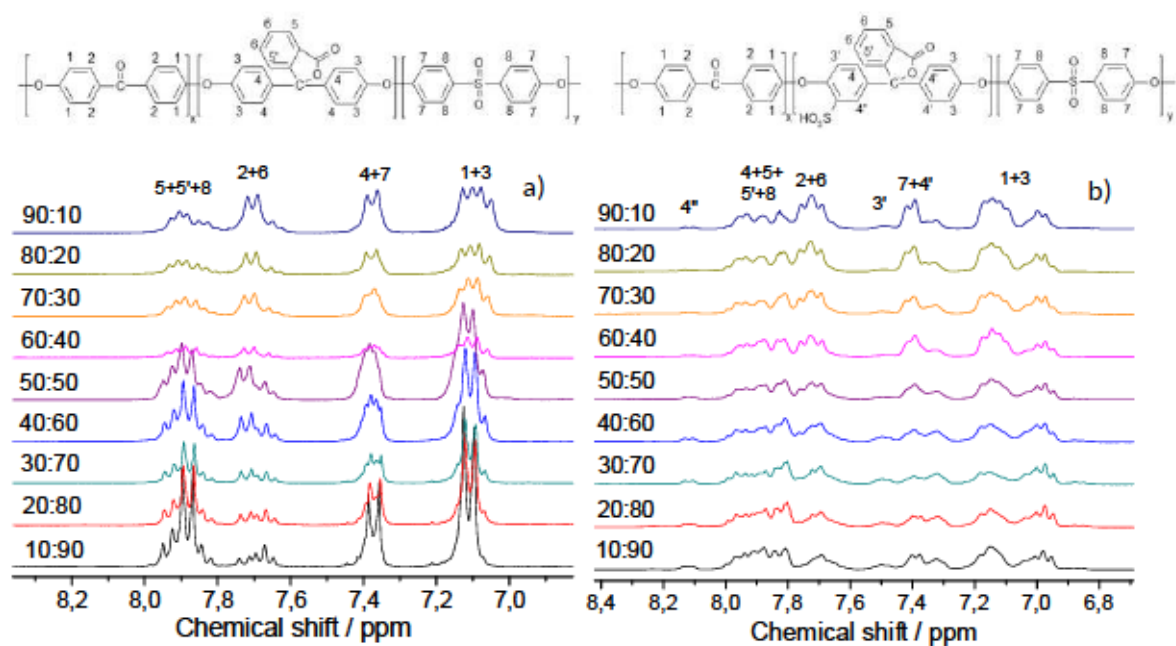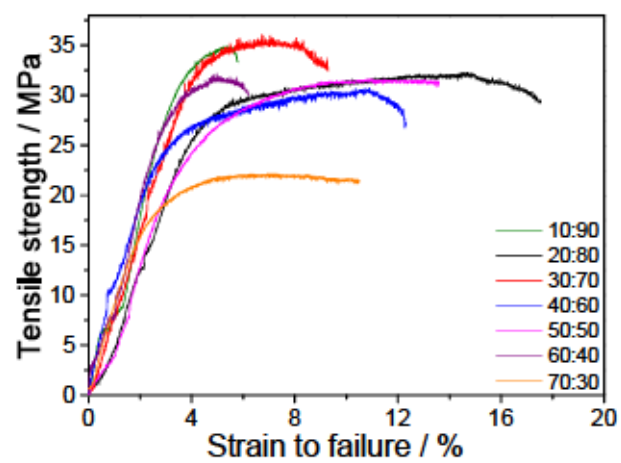
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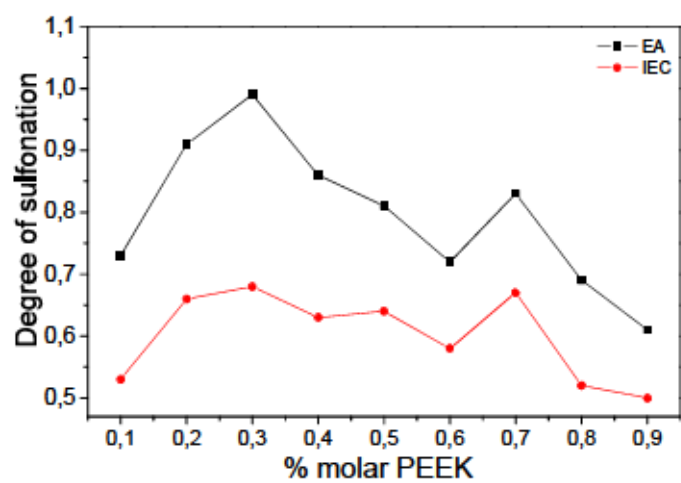
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Figure 4.

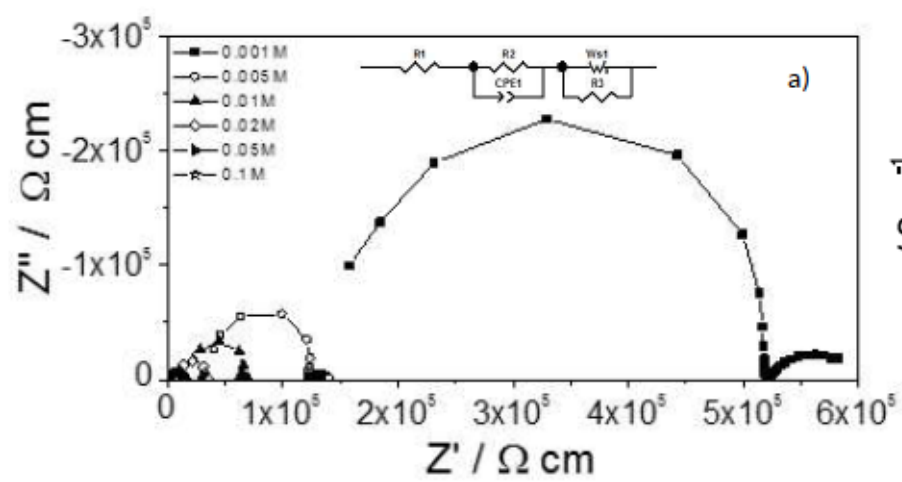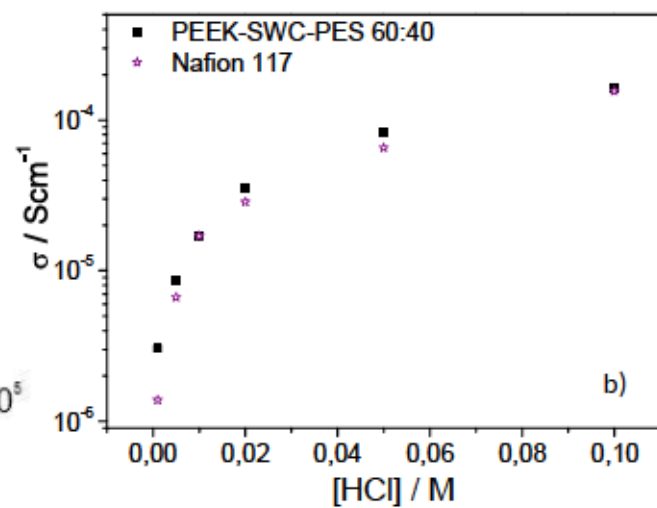**Figure 5.**

Figure 6.

Figure 7.

Figure 8.
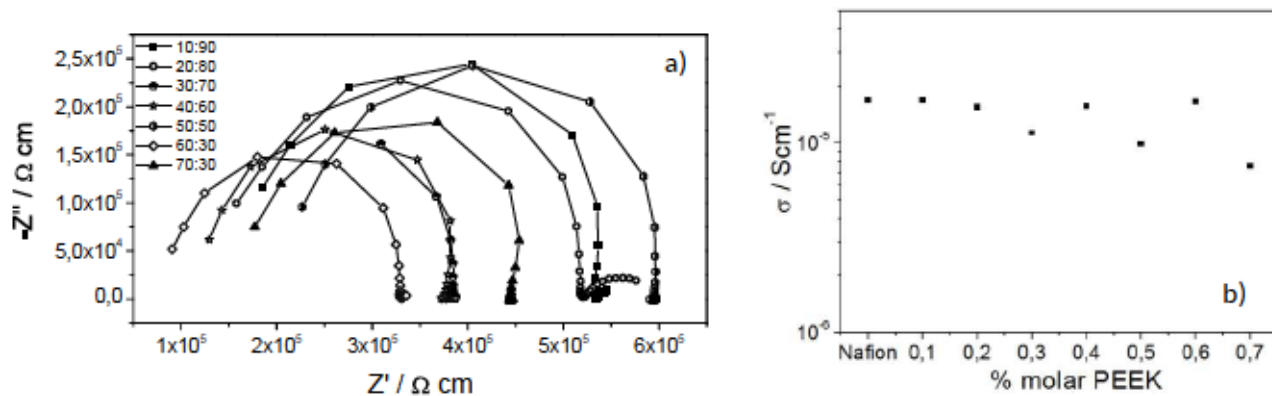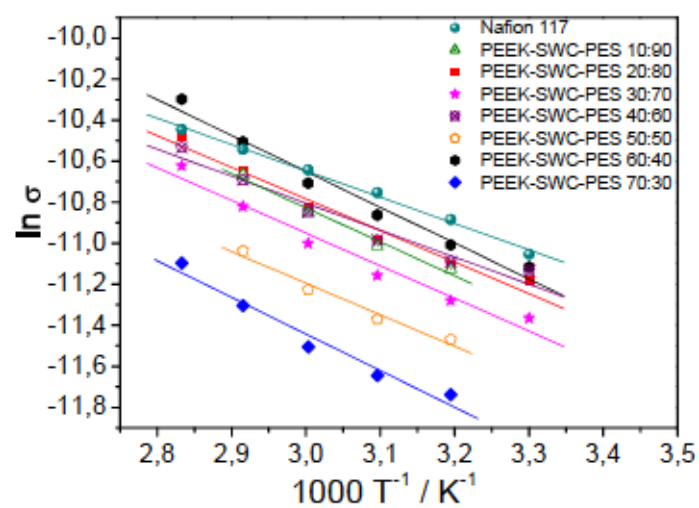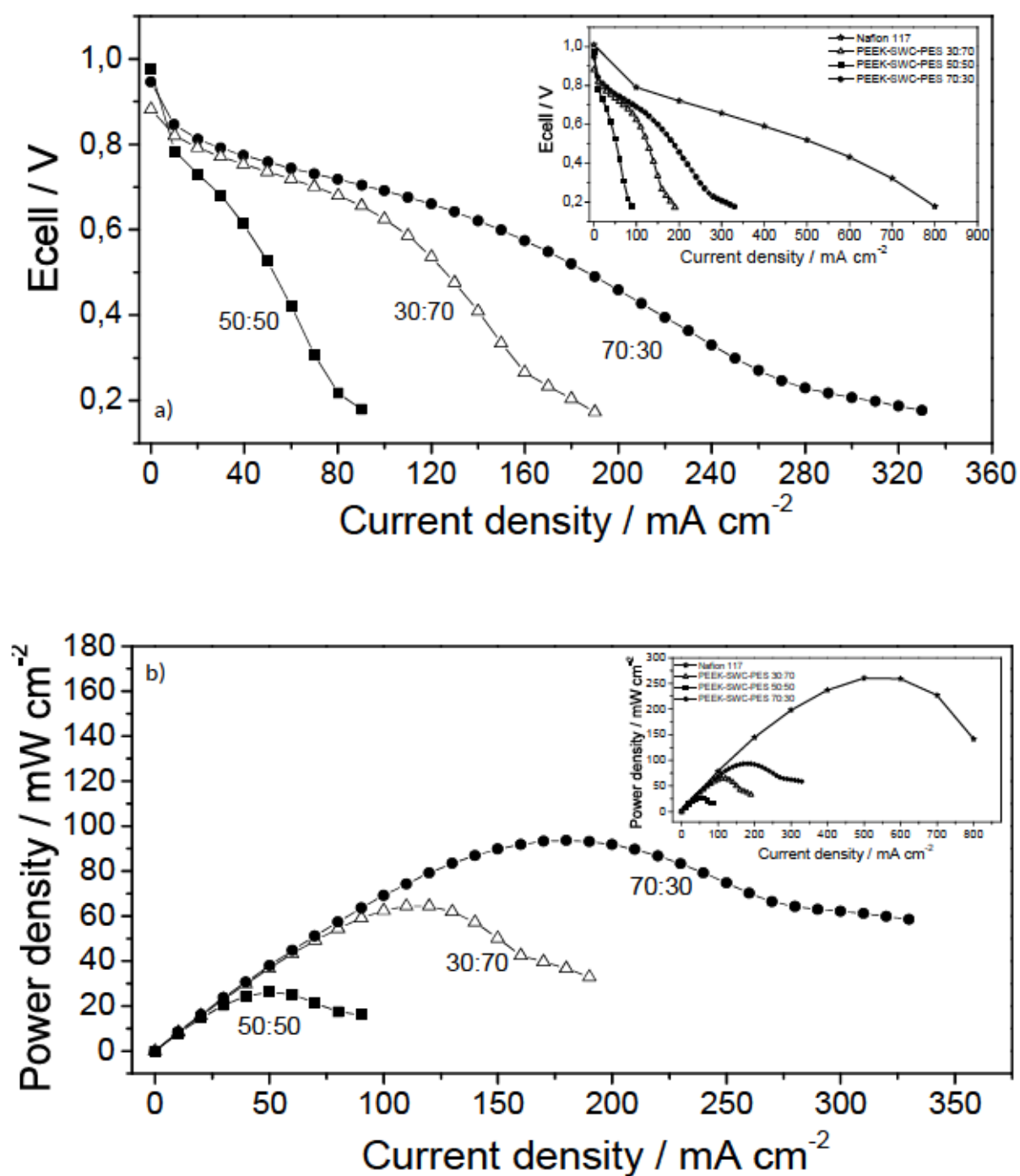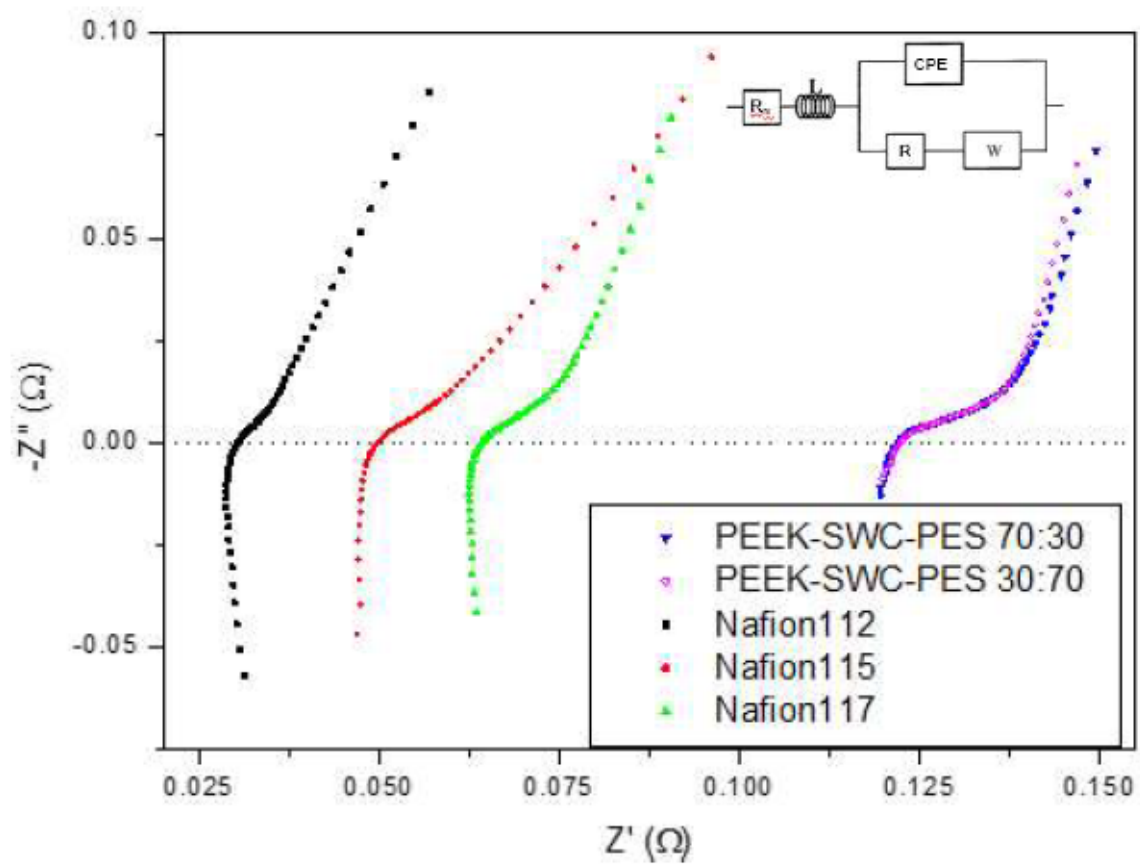
Figure 9.

Figure 10.

Figure 11.

Figure 12.

Highlights

• New sulfonated cardo PEEK-WC-PES copolymers were prepared and characterized.

• The prepared membranes showed suitable thermal and mechanical stability.

• PEEK-sWC-PES (70:30) membranes showed the best performance(current density 340mAcm^{-2})

• The low activation energy indicated a vehicular proton transport mechanism