Polymer modified sulfonated PEEK ionomers membranes and the use of Ru₃Pd₆Pt as cathode catalyst for H₂/O₂ fuel cells

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ABSTRACT

Nanocomposite membranes incorporating electrospun nanofibers of SPEEK, blended with 30 wt% PVB within a water-based matrix of SPEEK with 35 wt% PVA using water as solvent, were prepared and characterized for their application as Polymer Electrolyte Membrane Fuel Cells (PEMFCs) in H₂/O₂ operating at low temperatures. Compared with a dense bulk phase, an improvement of proton conductivity in the SPEEK-30PVB nanofiber framework was observed. The incorporation of the SPEEK-30PVB nanofibers provides mechanical improvement while the matrix phase of SPEEK-35PVA emphasizes the proton conductivity at crosslinking temperatures up to 140ºC. PEMFC performance tests showed promising results for the use of these novel low cost membranes. The nanocomposite membrane reached a power density 25% higher than the one of Nafion117 membranes with MEAs constructed with Pt loading in anode and in cathode. However, when the Pt of the cathode is substituted by Ru₃Pd₆Pt, the power density is lower in Nafion117 MEAs than in the nanocomposite. When used commercial Pt-carbon cloth (Pt-ETEK) for the electrodes, the power density achieved is 1.4 times higher for the Nafion117 MEAs than SPEEK nanocomposites. The differences observed in performance is attributed to the large polarization losses found in the composite membranes because of the interfacial phenomena associated with the use of commercial Nafion-based electrodes.

Keywords: PVB-Nanofibers, sulfonated PEEK, PEMFC performance, conductivity.

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1. Introduction

Recent studies have pointed out that proper water and heat management is one of the keys for achieving high power density performance and high energy efficiency in PEM fuel cells. Composite Nafion membranes using nanofibers such as PVA have proven to be efficient candidates as solid electrolytes for separating the anode from the cathode electrodes. This is possible because the incorporation of a nanofiber phase within the Nafion® matrix in thin membranes have produced significant savings in the consumed amount of Nafion polymer, keeping high performances and excellent mechanical properties [1,2]. On the other hand, it is known that conductivity and water uptake increase with the sulfonation degree [3-7], and the dependence of conductivity with water content is stronger for poly-ether ether ketone (SPEEK) materials than in the case of Nafion® [5,6]. In this sense, sulfonated SPEEK can be considered potential candidates to replace Nafion® membranes at a low cost, while exhibiting good chemical and thermal stabilities [1,2], what should enable operation at elevated temperatures in which electrochemical reaction rates speed up. The T_g values of SPEEK depend on sulfonation degree, i.e. ion-exchange capacity (IEC), and glass transition temperatures and it is usually found above 170ºC [1,3]. Therefore, SPEEK membranes have sufficient stability to operate at intermediate temperatures (120-130ºC) in PEM fuel cells.

Under certain conditions of temperature and sulfonation degree, the conductivity of SPEEK at high hydration levels surpasses the one of Nafion® (≈0.1 S/cm) [3-7]. Thereby, the use of SPEEK for PEMFC application, in which the fuel is supplied fully hydrated through the anode, can be very appropriate as membrane if the system is maintained at full hydrated conditions during a wide range of temperature and pressure conditions.

On the other hand, it is known that water uptake is a relevant key parameter for proton conductivity, methanol crossover and dimensional stability. Furthermore, it even influences in the long-term membrane electrode assembly (MEA) operation lifetime as during wet-up and dry-out cycles, the mechanical stability strongly depends on the swelling and contraction levels [8,9].

Methods to control water uptake involve polymer blending [10-15] and crosslinking, which can be carried out chemically [16-23] or ionically [24-27]. Other authors have also reported the possibility for additional self-crosslinking reaction in SPEEK via inter-chain polymerization of the sulfonic acid groups at high temperature under vacuum [28].

A peculiar characteristic of the hydrocarbon-type membranes is the fact that their properties become dependent on the pre-treatment and thermal history [4,29], as well as, on the solvent used for membrane casting [4,30-33]. In this regard, dimethylformamide (DMF) [30-32] and dimethylsulphoxide (DMSO) [33] are reported to affect very negatively to the performance of the membranes, while dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) solvents seem more appropriate to achieve better properties [30-32]. Interestingly, for the same membrane, IEC was found to be dependent on the membrane history, which has been explained through the peculiar morphology exhibited by the SPEEK materials -that is – narrower and shorter, less interconnected ionic channels for proton conduction than those found in Nafion® [9,34,35]. In previous works , it were found that PVB strongly reduced swelling, so a SPEEK grade with a high IEC value, 2.05 meq/g, was used. For the blend containing PVA, a SPEEK polymer with IEC value of 1.75 meq/g is the used for application in a PEMFC [5].

Another important issue that affects PEMFC performance is the MEA fabrication, which includes a catalysts-ink preparation process. This catalysts-ink preparation for MEA fabrication and its evaluation requires special skills, equipment and abundant reactant materials for use in chemical compositions [36]. Although, it has reported that fast screening techniques are more suitable to characterize the electrochemical behaviors of newly developed materials at the lab scale. The development of the most common technique for the MEA preparation was summarized by Schmidt and Gasteiger [37], and subsequently been improved by various research groups. The ink used to prepare MEAs follow different recipes, paying especial consideration on the weight ratio of the ionomer-to-catalyst loadeing at the cathode, where the thickness of the ionomer membrane, the fuel cell temperature, the nature of the gases (H_2/O_2 or H_2/Air), their humidity, and pressure are also variables which should be taken into account.

This work explores the preparation and characterization of different MEAs using membranes based on SPEEK with both a hydrophilic polymer (PVA) and a hydrophobic polymer (PVB), able to perform chemical crosslinking. Water solvent was selected for the casting preparation of the membranes and a pre-treatment step, consisting in the submersion of the membranes in boiling water for 1 hour was applied before further characterization. Finally a study of the membranes conductivity and fuel cell performance was conducted, and a comparison between our MEAs with MEAs using commercial electrodes and Nafion117 membrane was performed to complete the work.

2.   Experimental part

2.1. Materials

Granulated SPEEK (FUMION ionomers) with IEC of 1.75 and 2.05 mmol/g were acquired from Fumatech GmbH (St. Ingbert, Germany). Polyvinyl alcohol, (PVA) Mowiol 28-99 grade, and polyvinyl butyral, (PVB), were donated by Kuraray Europe GmbH (Frankfurt, Germany). Commercial polysulfone, was kindly supplied by BASF Española S.L. (Tarragona, Spain). Dimethylacetamide solvent was purchased from Acros Organics and anhydrous lithium chloride from Sigma-Aldrich. Commercial 20 wt% of 1 meq/g IEC Nafion® were acquired from DuPont Co. Finally Isopropanol extra pure and cetyl-trimethyl-ammonium bromide (CTAB) were purchased from Acros Organics, and 4-formyl-1,3-benzenedisulfonic acid disodium salt was acquired from Sigma-Aldrich.

2.2. Membranes preparation

2.2.1 SPEEK-30PVB nanofibers

Nanofiber mats of SPEEK-30PVB were obtained by electrospinning (YFLOW SL, Malaga, Spain). A potential difference of 35 kV was applied between the needle and the planar collector, which were separated 20 cm, and a flow rate of 0.5 ml h^{-1} of prepared solution was used for the electrospinning process. After 15 hours deposition the mat was crosslinked at 200 °C for 1 hour.

2.2.2. Composite membrane of SPEEK-35PVA reinforced with SPEEK-30PVB nanofibers

An initial solution of SPEEK in DMAc with 30 wt% of PVB (SPEEK-30PVB) was prepared as follows: a required amount of PVB was dissolved under stirring in DMAc at 80ºC for 1 hour. The solution was left to cool down at room temperature, afterwards, SPEEK (IEC = 2.05 meq/g) was incorporated and the mixture stirred for 1 hour at 80ºC until complete homogenization was reached (17.5 wt% total polymer concentration).

A water-based solution of SPEEK-35PVA (7.5 wt% concentration) was used. SPEEK with ion-exchange capacity (IEC) of 1.75 meq/g was dissolved in boiling water. An appropriate amount of PVA was separately dissolved in water at 80ºC (10 wt% PVA concentration), then, both solutions were mixed to prepare a SPEEK-35% PVA composition (wt. proportion), water was added until reaching a 7.5 wt% total polymer concentration.

The nanofibers (SPEEK-PVB) were immersed in this solution (7.5 wt% solution of SPEEK-35% PVA) for 5 minutes, thereafter placed in a climate-controlled chamber at 90ºC with very low

humidity for other 5 minutes. This process is repeated 4 times spinning 90º the nanofiber mats in each step. In the final step, the mat is left in the climate chamber for 10 minutes to enhance the drying of the newly formed composite membrane of (SPEEK-30PVB/SPEEK-35PVA). Then, the membranes were cutted along the frame borders and left at room temperature overnight to ensure total dryness.

Finally, 5x5 cm^2 membranes were cut and crosslinked at 140ºC for 1 hour in a hot-plate press under a pressure of 100 kg/cm^2. The prepared composite membranes were treated in boiled water for 1 hour, thereafter stored in distilled water at room temperature.

2.2.3. Nafion® membranes preparation

The procedure to prepare the Nafion® membranes has been similar to that used in previous work [1,2]. Briefly, the commercial 20 wt% of 1 meq/g IEC Nafion® was solvent exchanged by casting in order to prepare a 5 wt% solution in isopropanol/ water mixture, 4:1 w/w respectively. The 5% wt% of Nafion solution was used for the casting of pristine Nafion® membranes with thickness around 170 μm, specifically of 174±5μm. The thickness was controlled in function of the volume of solution loaded in Petri glass dishes and afterwards evaporated in an oven at 60 ºC overnight. The respective Nafion® membranes were annealed at 140 ºC for 90 min in the oven and then removed from the Petri dish by adding water. The last step was the conditioning of the membranes by treatment with water at 80 ºC for 30 min, followed by immersion in a 3 wt% hydrogen peroxide solution during 1 h at 80 ºC and further protonation at the same temperature by ion-exchange with a 1 M chlorhydric acid solution for another 1 h. Finally, the cast Nafion® membranes were washed with hot water at 80 ºC, dried and stored.

3.   Membrane characterization

3.1. Water uptake, swelling and ion-exchange capacity

Water uptake of the membranes was measured by drying H$^+$-form samples in a vacuum chamber and after weighed the dry membranes (W_d). Then, they were immersed in distilled deionized water overnight. Afterwards membranes were removed from water, gently dried with filter paper to remove excess surface water, and then weighed again (W_w). This operation was five-folds repeated. Water uptake was obtained by means of the expression (1) and the values referred to the dry membrane are given in Table 1.

$$Water\ uptake(\%) = \left(\frac{W_w - W_d}{W_d}\right) \cdot 100 \qquad (1)$$

The swelling degree in-thickness were also calculated with a similar expression considering the wet thickness L_w, below the same degree of hydration conditions above mentioned for the nanocomposite respect to the dry measurement, L_d.

$$Thickness\ swelling\ (\%) = \left(\frac{L_w - L_d}{L_d}\right) \cdot 100 \qquad (2)$$

The ion-exchange capacity (IEC) was obtained by immersing the membranes in the acid form in 0.1 M HCl solution for 12 hours. The acidic membranes were further washed several times with distilled water and then immersed into a 1 M NaCl solution. The protons liberated in the exchange reaction $R\text{-}H + Na^+ \rightarrow R\text{-}Na + H^+$ were titrated with a 0.01 M NaOH solution to determine the concentration of exchanged protons. IEC was obtained as

$$IEC\ (eq/kg) = \frac{V_{NaOH} \times 0.01}{m_d} \qquad (3)$$

where V_{NaOH} and m_d are, respectively, the volume in liters of NaOH solution spent in the titration of the protons released expressed as meq H^+ / g of wet polymer. IEC is usually given in equivalent/kg of dry membrane. In this case, equation 1 uses m_d as reference since IEC is a property related to the chemical structure of the polymer.

3.2. Mechanical properties

Static tensile strength tests were carried out at 25ºC using a DMTA Q800 TA Instruments. Tension clamp membranes were subjected to a controlled force of 1lb/inch. The speed rate was fixed at 1N/min with a preload of 0.001N. A crosshead rate of 0.4mm/min collecting data each 500 ms was used in each measurement. The separation between the clamps was fixed at 10 mm and the maximum exerted force was set at 2kN with an initial static force of 0.1 N. The samples were cutted in pieces of approximately 0.2x2x10 mm, measurements of thickness and width were conducted by means of a length calibrator. All the measurements were performed at ambient temperature (around 25ºC). The membrane thickness was calculated from the average value of five measurements on different parts of the sample, and its uncertainty is represented by the standard deviation obtained. Before performing tension-stress experiments the surface of the membranes were dried through filter paper and pressed between two sheets of acetate. Afterwards the membranes were dried at 35ºC for 4 days.

3.3. Membrane conductivity

The conductivity of the membranes was measured by impedance spectroscopy at different temperatures, in the frequency range $10^{-1} < f < 10^7$ Hz with 0.1V amplitude, using a Novocontrol broadband dielectric spectrometer (Hundsangen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface. For this, the membranes were previously immersed in bi-distilled water and sandwiched between two gold electrodes in a liquid parallel plate cell coupled to the spectrometer; deionized water was incorporated to ensure a full hydration of the samples below 100ºC and in equilibrium with its vapor above 100ºC. To see the reproducibility of the measurements, all of them were repeated three times. The temperature was controlled by nitrogen jet (QUATRO from Novocontrol) with a temperature error of 0.1 K during every single sweep in frequency. The thickness of the membranes was measured in dry and wet conditions with a micrometer, taking the average of ten measurements at different parts of its surface.

4.   Catalyst synthesis and characterization

The Ru_3Pd_6Pt was synthesized by chemical reduction with $NaBH_4$ following a methodology previously reported for the synthesis of nanocatalysts materials [38,39]; briefly, the $RuCl_3$ (Aldrich, 0.114 mM), $PdCl_2$ (Aldrich, 0.228 mM), and H_2PtCl_6 (Aldrich, 0.023 mM) were solvated in THF (Aldrich) at 60°C under vigorous stirring, maintaining the nitrogen flux above the solution. Then the reducing agent $NaBH_4$ (33 mM) was slowly added to the solution, a color change indicates that the reduction was completed, as previously reported. The reaction products were washed several times with tri-distilled water and acetone (Aldrich) to remove the byproducts of the reaction and traces of the solvent. Afterwards the powders was dried at 60 °C for overnight and dispersed at 40% on Vulcan® carbon using an ultrasonic bath.

The catalyst was physically characterized by X-ray diffraction (XRD) using an X'Pert PRO PW3040 (PANalytical) diffractometer with monochromatic Cu Kα1 radiation (λ = 1.54 Angstroms) in a 2θ range from 20 ° to 90º with a step width of 0.2 ° min^{-1}. The morphology of the material was analyzed using a Carl Zeiss (GEMINI FESEM) microscope operated at 15 kV. Particle size was determined from transmission electron microscopy (TEM) analyses, using a 2200FS microscope, operated at 200 keV and equipped with energy dispersive spectroscopy (EDS) used to obtain an average and local chemical composition of the samples. After physical characterization, the catalytic

activity for the oxygen reduction reaction (ORR) on Ru_3Pd_6Pt was evaluated in a 0.5 M H_2SO_4 electrolyte at 25 °C by rotating disk electrode (RDE) technique. Electrochemical experiments were performed in a conventional single-compartment three-electrode electrochemical cell using a potentiostat/galvanostat (PARSTAT model 2273).

5.   Membrane Electrode Assembly (MEA) preparation

The catalysts-ink preparation for the MEA fabrication was determined following the briefly described procedure: cathodic catalytic inks were prepared by mixing and sonicating during 20 seconds a suspension formed by 10 mg of electrocatalysts (Ru_3Pd_6Pt/C or commercially available Pt/C), 83 μL of Nafion ® ionomer (5 wt. %, Du Pont 1000EW) and 1.5 mL of ethanol in order to have 20 wt.% in relation to the total catalyst loading, later, the slurry was immediately used for MEA preparation. The casting was carried out using the Catalyst Coat Substrate (CCS) method by air brushing the ink onto a gas diffusion layer (GDL), followed by drying at 80 °C for three minutes.

The fuel cell performance of the MEAs was determined in a Compucell GT, Electrochem 890B commercial system, as described elsewhere [40, 41]. Briefly, the fuel cell test station was operated at 100 cm^3min^{-1} flow of high purity H_2 and O_2 in anode and cathode, respectively. The gas pressures at the anode and cathode sides were set at 2 bar. Humidification of the reactant gases was ensured by bubbling them in distilled water at 85 ºC. Comparison measurements were also carried out using commercial Nafion® 117 membranes (DuPont Co.).

6.   Results and discussion

Following the procedure described in previous works [5] we have found that PVB strongly reduced swelling, so a SPEEK grade with a high IEC value, 2.05 meq/g, was used to build nanofibers with PVB due to its higher degree of sulfonation. For the blend containing PVA, a SPEEK polymer with IEC value of 1.75 meq/g was employed for application in PEMFC because a rubber-like phase was formed where swelling and water uptake was large, but limited enough to allow the formation of stable membranes. We have observed that swelling and water uptake parameters diminish with increasing crosslinking temperature and converge at 140 ºC [42]. Consequently, this work consider this crosslinking temperature to build our nanocomposite membranes used for implementation of

assemblies for PEMFC applications. Table 1 lists the swelling degree, water uptake and IEC parameters of the nanocomposite and Nafion117 membranes.

Table 1. Swelling (through thickness) of the nanocomposite membranes together with water uptake and ion-exchange capacity (IEC) are reported as function of crosslinking temperature after 1 hour in boiling water. Membrane thickness is given in dried state as a reference. The last columns present the average values of Young's modulus (E), ultimate tensile strength (σ_{ult}) and tensile rupture strain (ε_r).

Membranes	Thickness in dry form (µm)	Thickness after swelling (%)	Water uptake (%)	IEC (meq·g^{-1})	E (GPa)	(σ_{ult}) (MPa)	ε_r (%)
Nanocomposite	70±5	20±3	51±5	0.55±0.01	1.2±0.3	50±10	15±5
Nafion-117*	174±5	24±3	21.5±1	0.91±0.01	1.8±0.2	42±8	14±5

* membrane was prepared by casting.

Static mechanical testing was performed on samples crosslinked at 140ºC of nanocomposite membranes with the aim to estimate and compare their mechanical properties with membranes prepared with Nafion-117 by casting. Special interest was placed in evaluating the mechanical reinforcement effect of the nanofibers. Mechanical parameters such us Young's modulus, ultimate tensile strength, and tensile rupture strain were obtained and are reported in Table 1. A close inspection of these values, in the case of fully hydrated conditions, reveals that nanocomposite membranes have a smaller Young's modulus than Nafion-117 membranes, which may be a consequence of the difference in thickness; however, the ultimate tensile strength (σ_{ult}) is about 20% higher in case of nanocomposite than in a Nafion membrane. The tensile rupture strain (ε_r) for both membranes are practically insignificant. Unfortunately, the available experimental setup did not allow guaranteed evaluation of the samples in a fully hydrated state.

Figure 1a shows an X-ray diffraction pattern of Ru_3Pd_6Pt; this pattern exhibits at least five diffraction peaks at 2θ values of 40°, 47°, 67°, 81°and 87°. The characteristic reflection peaks, were matched with JCPDS data files, 01-065-2867 to Pd, 01-065-2868 to Pt and 01-065-7646 to Ru; none peak matches exactly with Pd or Pt values indicating these peaks could be phases of three-metallic catalyst, these peaks had been also observed for this three-metallic catalyst previously synthesized by another techniques [43,44]. A SEM image of the synthesized powder catalyst is shown in Figure 1b.

The morphology of the catalyst produced shows the presence of large agglomerates. Each of these agglomerates consisted of very small and irregular clusters. Figure 1c shows a TEM image of agglomerated particles containing small homogeneous particles in nanometric size (less than10 nm) with spherical morphology, similar results in particle size and morphology to those reported previously for this material [43,44]. The inset in Figure 1c shows the corresponding selected area of diffraction patterns. These particles were analyzed by EDS, resulting a composition of 33.1 at % Ru, 56.1 at % Pd and 10.8 at % Pt (Ru_3Pd_6Pt), in concordance with the started estimated composition of synthesis.

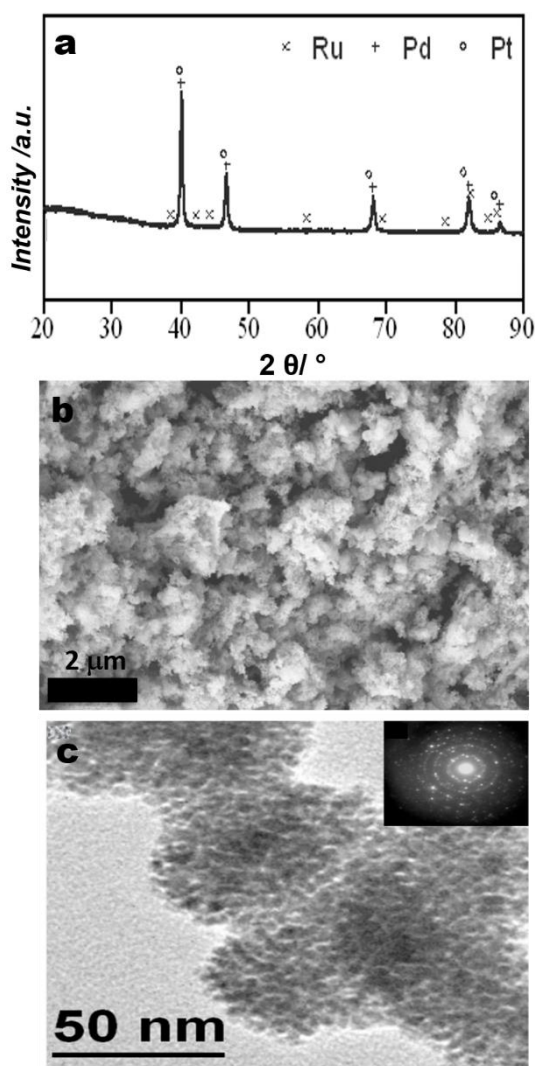Figure1. (a) X-ray diffractogram, (b) SEM micrograph, and (c) TEM image of as-synthesized Ru_3Pd_6Pt catalyst. The inset in Figure 1c shows the corresponding selected area of a crystalline pattern.

The characteristic ORR polarization curves from RDE measurements at different rotation rates, of nanometric Ru_3Pd_6Pt/C is summarized in Figure2a. At the beginning of the scan potential in

the negative direction from the open circuit potential, 0.97 V/NHE, a defined charge transfer control is observed in the region where the current density is independent of the electrode rotation speed. The mixed kinetic-diffusion control region (0.8 to 0.75V/NHE) is followed by the appearance of a diffusion limiting current region. With increase of the rotation rate, currents also are raised due to an enhancement of the oxygen diffusion through the thin film electrode surface. According to these behaviors, the overall measured current of the oxygen reduction can be considered to be dependent on the kinetic current and the diffusion-limited currents.

Figure 2b presents the Koutecky-Levich plot which shows a linear relationship between the diffusion current density (j^{-1}) and the inverse square root of the rotating speed ($\omega^{-1/2}$). This behavior indicates a first order kinetics of the Ru_3Pd_6Pt with respect to the ORR within the potential range studied. The slope in the Koutecky-Levich plot illustrates that the number of electrons involved in the oxygen reduction, is n=4e⁻, corresponding to the reaction $O_2 + 4H^+ + 4e^- \rightarrow H_2O$. The catalytic activity of a material can be measured in terms of parameters deduced from the mass transfer-corrected Tafel slope (not included). The values obtained for this catalyst were: Tafel slope (-b) at about $46.6 mVdec^{-1}$, exchange current density (j_0) of $3.1 \times 10^{-5} mA\ cm^{-2}$, and charge transfer coefficient (α) of 0.55. Based in the electrocatalytic behavior, it was considered that Ru_3Pd_6Pt is a good candidate to be used as a cathode electrode in a MEA enhanced with nanocomposite membranes. These parameters are in the range of that reported for this catalyst synthesized by microwave and poliol techniques [43,44].
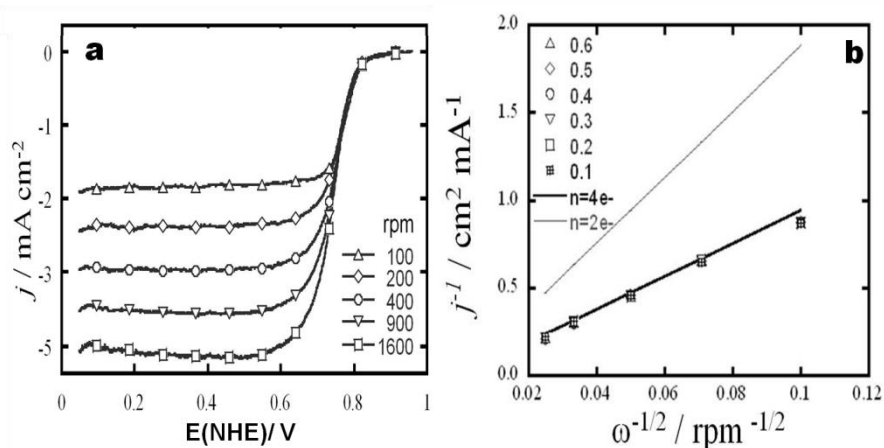

Figure 2. (a) Steady-state polarization curves for the ORR on Ru_3Pd_6Pt in 0.5M H_2SO_4, and (b) Koutecky-Levich treatment.

PEMFC performance was evaluated from 25 to 80ºC with 100 cm^3 min^{-1} flow of high purity H$_2$ and O$_2$ in anode and cathode, respectively. The gas pressures at the anode and cathode sides were set at 2 bar. Humidification of the reactant gases was ensured by bubbling them in distilled water at 85 ºC. The performance of MEAs prepared with nanocomposite SPEEK 30PVB/SPEEK 35PVA and Nafion-117 membranes were measured in a single cell operating with H$_2$/O$_2$ at 25, 40, 60 and 80ºC. The polarization curves are shown in Figures 3, 4 and 5, where a fixed temperature of 80 ºC was used. An open circuit voltage (OCV) of approximately 1.0 V was found for all MEAs build with Nafion-117, which is a well-known typical value for Nafion® membranes, and a slightly lesser value was found for the nanocomposite membrane. The cell voltage of a PEM fuel cell can be modeled by means of eq. (4) as reported by several authors [40-42,45,46].

$$V = V_{OC} - A \cdot \ln\left(\frac{i}{i_0}\right) - i \cdot R \cdot S \tag{4}$$

where V is the cell voltage, V_{oc} the reversible open circuit voltage, i the cell current density, i_0 the forward and reverse (exchange) current density at equilibrium in OC conditions, R is the ohmic resistance of the MEA, S the area of MEA exposed to proton flux. A is the sum of the slopes of Tafel equation for anode and cathode. The Tafel slope can be given by $A = \frac{RT}{2\alpha F}$, where α is the charge-transfer coefficient, R the gas constant, T the absolute temperature and F the Faraday's constant. A fit of equation (4) to the experimental values showed in figures 3, 4 and 5 can be used to obtain the values of V_{0C}, A, i_0 and R, respectively. For this we have fitted the experimental results of the performance by GRG nonlinear algorithm and the resulting fitting parameters are shown in table 2.

Table 2. Fitting parameter results for the experimental I-V curves and maximum power density for the Membrane Electrode Assemblies (MEAs) at 80ºC.

MEAs	V_{OC} (V)	A (mV)	α	i_0 (mA cm^{-2})	R (Ω cm^2)	P_{max} (W cm^{-2})
MEA1						
Nanocomposite	0.802	39	0.39	0.12	0.88	145
Nafión-117	0.902	45	0.34	0.10	0.68	190
MEA2						
Nanocomposite	1.050	42	0.36	0.37	0.80	375
Nafión-117	0.986	58	0.26	0.31	0.44	300

MEA3						
Nanocomposite	0.995	45	0.34	0.15	0.65	260
Nafión-117	1.009	64	0.24	0.09	0.42	350

MEA1 consists of an assembly prepared with Pt for the anode and Ru_3Pd_6Pt as cathodic catalyst. MEA2 has only platinum as catalyst, and was used for reference. MEA3 was prepared with a commercial Pt (E-Tek) catalyst used on the anode and cathode sides. A comparison of the MEAs voltage when the current density was 50 mA cm^{-2} shows the following tendency: MEA2>MEA3>MEA1. When comparing the results of the nanocomposite MEA2 and the MEA with Nafion-117 membranes working at 80ºC, the corresponding voltage for 50 mA cm^{-2} is higher for the MEA2 of SPEEK-30PVB/SPEEK-35PVA than for the Nafion-117 membrane, however this performance is opposite for the MEA1 and MEA3.

Figure 3 shows the cell performance for the assembly prepared with Pt as anode catalyst and Ru_3Pd_6Pt in the cathodic side, evaluated at 80°C and 2 bar of pressure. A decrease of almost 0.1 V in open circuit potential is observed when the Nafion117 membrane is substituted for a SPEEK-30 PVB/SPEEK-35PVA membrane. A decrease in the i_{max} is also observed near the 50 mW cm^{-2}.

In order to compare the results obtained between the membranes based SPEEK and Nafion®, assemblies with Pt/Pt as catalysts in both anode and cathode sides, they were prepared under the same pressing and temperature conditions and the results obtained are shown in Figure 4. In this figure it is observed a maximum power density close to 375 mW cm^{-2} for the SPEEK membrane, indicating a considerable increase of the performance over that of Nafion®, which exhibits only 300 mW cm^{-2}. This difference can be attributed to the difference in thicknesses of the membranes. Figure 5 shows the comparison between the nanocomposite membranes based SPEEK and Nafion® using commercial assemblies with Pt (E-Tek) assemblies. In this figure, it is observed a maximum power density close to 350 mW cm^{-2} for the Nafion-117 membrane at about of 750mA cm^{-2} of current density. However the nanocomposite membranes reach the value of 260 mW cm^{-2} with a current density of 570 mA cm^{-2}.
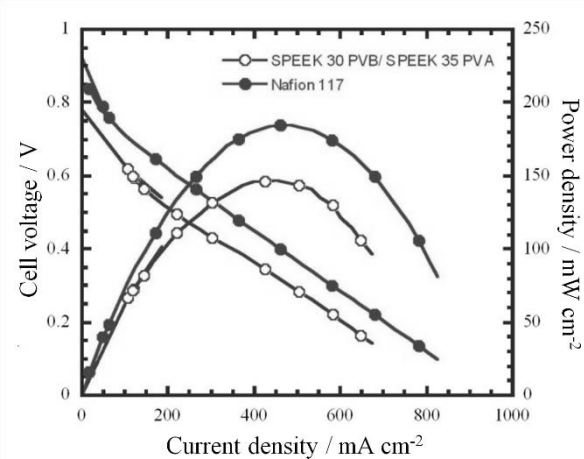
Figure 3. Polarization curves (Cell voltage, V, on the left axis and Power density P=iV on the right axis, as a function of Current density, i) of MEAs fed with H_2/O_2 at 80 °C and 30 psi with Pt anode and cathode Ru_3Pd_6Pt .
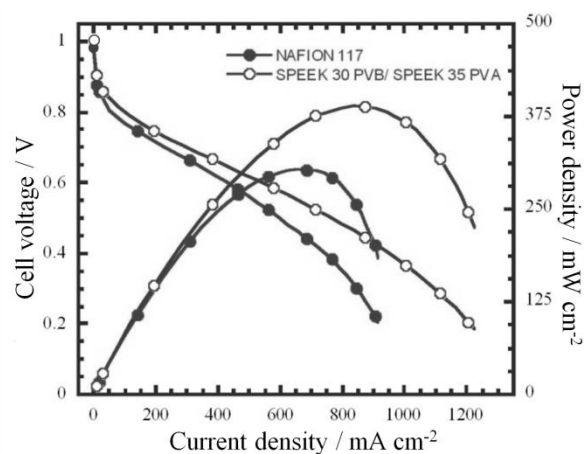

Figure 4. Polarization curves (Cell voltage, V, on the left axis and Power density P=iV on the right axis, as a function of Current density, i) of MEAs fed with H_2/O_2 at 80 °C and 30 psi with Pt anode and cathode Pt.
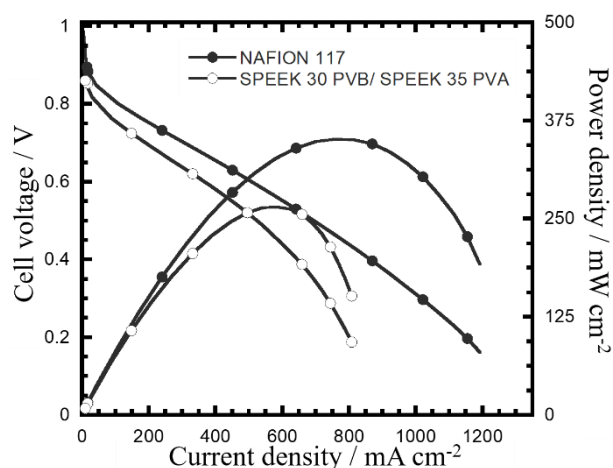

Figure 5. Polarization curves (Cell voltage, V, on the left axis and Power density P=iV on the right axis, as a function of Current density, i) of MEAs fed with H_2/O_2 at 80 °C and 30 psi with anode and cathode Pt E-Tek.

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In figure 5 the performance of the membranes using commercial electrode assemblies is presented, it should be noted that these MEAs were not pressed. In the figure, V_{OCV} are close for both membranes, and the differences of maximum power (P_{MAX}) (50% Nafion®/SPEEK) are lower than those registered with the trimetallic electrocatalyst. These results indicate that the composition of the catalytic ink must be improved to optimize the performance results, using the same composition of ionomer to the composite membranes instead of the commercially available Nafion® monomer.

The Tafel slopes, A, is higher for all MEAs with a Nafion-117 membrane as polyelectrolyte. These results could be related with the thickness, where in case of Nafion-117, the membrane is about 2.5 fold thicker than nanocomposite membrane. This result is consistent with the observations made by other researchers [47-49]. The oxygen reduction reaction at the cathode is influenced by the proton transport limitation associated with the ionic resistance of the membrane, which is dependent of its thickness. The value of the charge transfer coefficient, α, is lower than the standard value accepted for electrochemical reactions in PEMFCs [50]. However, it is in the range of the estimated values from experimental PEMFC polarization curves [51, 52] (see Table 2). The resistances of the MEAs are quite similar to the resistance of the membranes measured by impedance spectroscopy. From the values obtained for the membranes forming the MEA1, it was estimated that the nanocomposite conductivity was about 0.008S/cm while for the Nafion-117 membrane, its value was 0.026 S/cm, approximately three times higher.

7.   Conclusions

This study found that formation of nanofiber morphology with the SPEEK-30PVB system improves the proton conductivity about one order of magnitude if we compare with the same composition in a dense bulk phase.

The incorporation of SPEEK-30PVB nanofibers into the water-based SPEEK-35PVA matrix provides membranes where the proton conductivity remained high. The mechanical properties of the nanocomposite membranes are adequate for application in PEMFC and DMFCs.

Notably, performance of the nanocomposite membranes was strongly influenced by electrochemical polarization losses when commercial electrodes incorporating Nafion® as ionomer were used, and compatibility issues were involved. Our results show that although the composite membranes do not reach the performance of Nafion®, they represent a viable alternative to it. It is

proposed that by changing the composition of the catalytic ink (replacing the Nafion® ionomer with one used for the composite membrane), performance of MEAs which use trimetallic electrocatalysts can be optimized.

This work shows one promising approach to obtain novel membranes prepared from low cost materials with properties close to Nafion®, and optimal characteristics for fuel cell applications at temperatures between 50 to 130ºC.

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