



Proton conducting sol–gel sulfonated membranes produced from 2-allylphenol, 3-glycidoxypropyl trimethoxysilane and tetraethyl orthosilicate

J. Mosa*, A. Durán, M. Aparicio

Instituto de Cerámica y Vidrio (CSIC), C/Kelsen 5, Campus de Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

An important research area in proton exchange membrane fuel cells (PEMFC) is devoted to the development of low cost membranes able to work at temperatures higher than 100 °C. In this work, homogeneous, transparent and crack-free hybrid membranes have been synthesized using tetraethyl orthosilicate (TEOS), 3-glycidoxypropyl trimethoxysilane (GPTMS) and 2-allylphenol (AP) as precursors. The synthesis of proton conducting membranes was performed by a post-sulfonation method using trimethylsilyl chlorosulfonate as a mild sulfonating agent. The water retention properties provided by sulfonate and hydroxyl groups and the high porosity leads to relatively high proton conductivity (maximum values around $1.3 \times 10^{-3} \text{ S cm}^{-1}$ at 140 °C and 100% RH) for membranes treated at 180 °C and sulfonated for 2 h.

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1. Introduction

The proton exchange membranes fuel cells (PEMFC) technology is receiving a great deal of attention last years because of their advantages over other type of fuel cells [1–3]. The PEMFCs are at present used at temperatures lower than 80 °C because the perfluorosulfonic acid membranes have to maintain a relative humidity (RH) close to 100%.

One of the important areas of research interest in PEMFC is the development of a low cost membrane for high temperature operation (100–150 °C), with little or null dependence on humidity [4,5] to improve energy conversion efficiency and to avoid CO poisoning of catalysts. Organic–inorganic hybrid materials are viewed as the next generation materials in many applications because they offer the possibility of combining the properties of two components in a unique material at molecular level, hence to develop functional materials with tuned properties [6]. New generation electrolytes must, in fact, meet several requirements: among them, most important are high proton conductivity, sufficient flexibility to make good contacts with electrodes and, at the same time, enough rigidity to support the membrane electrode assembly (MEA), high hydrolytic stability, and low permeability to fuels [7–9]. Modulation of the

properties of the final materials can be achieved by suitable rate of the inorganic and organic components.

Sulfonation is a powerful and versatile process, frequently used for polymer modification to improve hydrophilicity and other membrane properties such as higher water flux, permeability and proton conductivity at the same time [10]. Generally, there are two methods to introduce the sulfonate groups onto polymer chain: post-sulfonation of polymer and direct copolymerization with sulfonated monomers. In the former method, the sulfonate groups can be easily attached onto polymer chains by using appropriate sulfonate agents [11]. Since sulfonation is an aromatic electrophilic substitution reaction (SE_{ar}), electro-donating substituents favour the reaction whereas electron-withdrawing groups do not. 2-allylphenol (AP) is easy to sulfonate because hydroxyl groups activate aromatic ring for electrophilic substitution in ortho- and para-positions, whereas the allyl group activates meta-positions. Sulfonation of AP has been conducted in heterogeneous media with different sulfonation agents, HClSO_3 and $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ in CH_2Cl_2 . HClSO_3 was chosen due to its simplicity, adaptability and reactivity; however, cross-linking and degradation side reactions sometimes happen and sulfonation degree is difficult to control [12]. During the sulfonation reaction, it is possible to affect or even destroy completely the bead morphology due to the action of sulfonating agent and reaction conditions. Trimethylsilyl chlorosulfonate does not usually induce chain cleavage, even at high sulfonation degree, but its efficiency is lower than HClSO_3 .

In this study, we prepared novel organic–inorganic hybrid membranes using a combination of sol–gel route and organic

* Corresponding author. Tel.: +34 91 735 58 40; fax: +34 91 735 58 43.

E-mail addresses: jmosa@icv.csic.es (J. Mosa), aduran@icv.csic.es (A. Durán), maparicio@icv.csic.es (M. Aparicio).

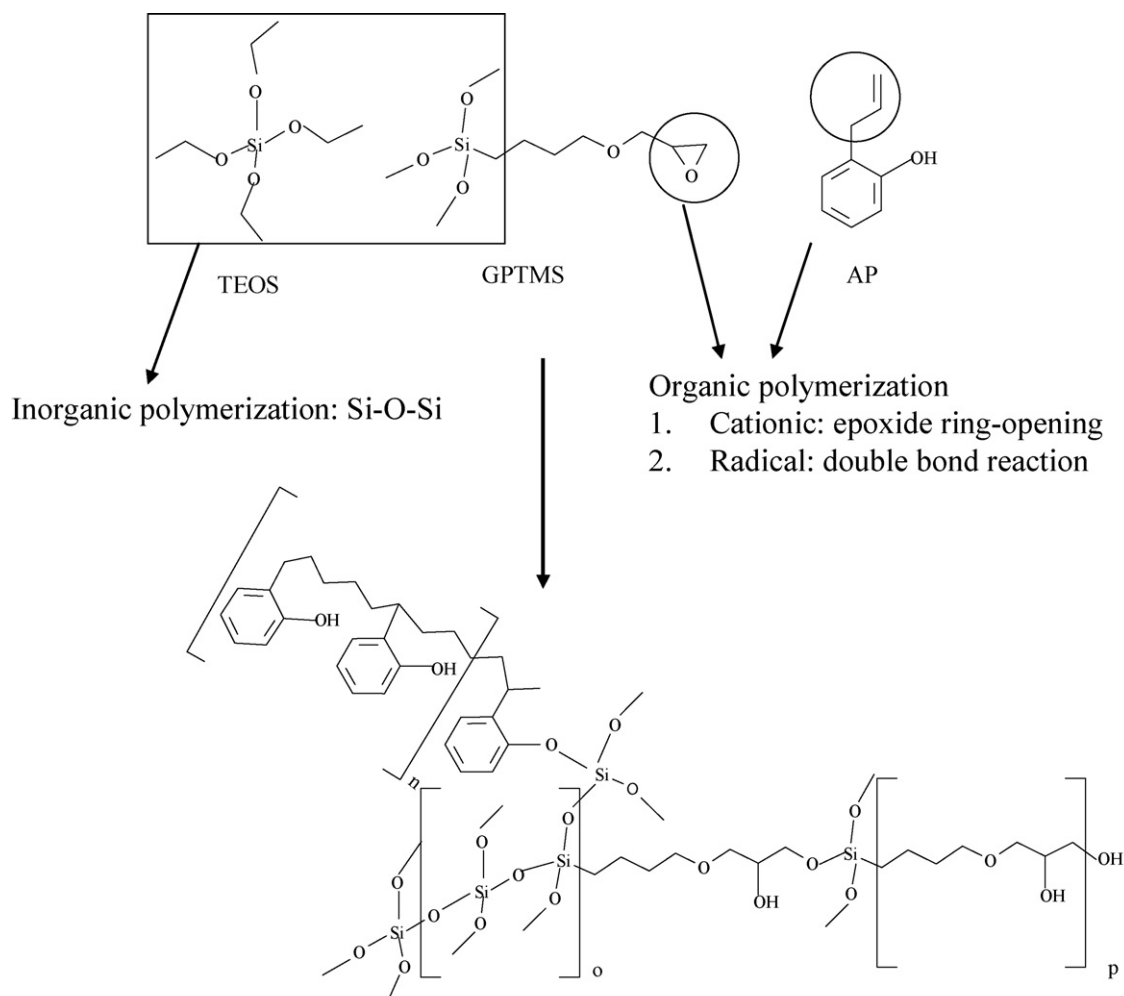


Fig. 1. Sol-gel precursors and monomers used in the synthesis of epoxy based hybrid organic-inorganic membranes and polymerization reactions involved.

polymerization. The strategy chosen was to prepare a covalent hybrid polymer, where SO_3^- units were expected to enhance the proton conductivity. Nevertheless, the degree of sulfonation must be controlled because mechanical, morphological and solubility properties progressively deteriorate with increasing sulfonation reaction [13]. The proton conduction mechanism of sulfonated polymers is, in fact, water assisted, and thereby their hydration state is a crucial factor for good electrochemical performance [14].

The present work presents the synthesis of hybrid membranes prepared with tetraethyl orthosilicate (TEOS), 3-glycidyloxypropyl trimethoxysilane (GPTMS) and 2-allylphenol. The polymer component was directly bonded to the inorganic component through the epoxy ring-opening and radical organic polymerization of AP under acid conditions. On the other hand, inorganic polycondensation reactions of alkoxy groups from GPTMS and TEOS with the reactive OH groups of AP were carried out. We expect that the Si-O-Si backbone, that provides thermal stability, mechanical strength and a swelling reduction, will be connected with the organic component by the pseudo PEO-chain, which provides good flexibility and processibility. Moreover, AP improves the proton conductivity due to sulfonate groups that can be attached to it and increases the hydrophilic behaviour of the membrane by their lateral OH group.

Optimal sulfonation time to promote proton conductivity, avoiding swelling process are evaluate in this work. SEM, TGA-DTA, FTIR, water adsorption, ion exchange capacity and EIS techniques have been used for characterising the obtained membranes.

2. Experimental

Tetraethyl orthosilicate and 3-glycidyloxypropyl trimethoxysilane from ABCR, and 2-allylphenol from Fluka were used as precursors (Fig. 1). This figure also shows the polymerization reactions (inorganic and organic) involved in the synthesis of the hybrid network. The sol (molar composition: 20 TEOS-40 GPTMS-40 AP) was prepared by mixing absolute ethanol (molar ratio ethanol/AP=2), AP and 2,2'-azobis(isobutyronitrile) (AIBN, from FLUKA) (0.85 wt% respecting to AP) as initiator of the free-radical copolymerization. The mixture was stirring at room temperature for 30 min. Subsequently, GPTMS and TEOS were incorporated in the solution stirring at room temperature for 15 min. Then, water as HCl 0.1 N (molar ratio of water/TEOS+GPTMS=3.5) was added drop by drop. The resulting homogeneous and transparent solution was stirred for 60 min. The sol was cast in polytetrafluoroethylen moulds and left at 60 °C for obtaining homogeneous gels through co-polymerization of AP and GPTMS, and simultaneous sol-gel reactions of TEOS and GPTMS. Hybrid membranes were additionally treated at 110 or 180 °C (heating rate 0.1 °C min⁻¹) in air for 2 h to complete drying and curing. The membranes were sulfonated by immersion between 2 and 24 h in 0.3 M solution of chlorosulfonic acid (HSO_3Cl) and trimethylsilyl chlorosulfonate ($(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$) (from Panreac and Aldrich, respectively) in 1,2-dichloroethane.

The fracture surface of the membranes was observed with a HITACHI S-4700 field emission scanning electron microscope (FE-

SEM). Elemental analysis by EDX (NORAN system six) was used to study the distribution of elements across the membrane thickness. Thermal stability of the membranes dried at 110 and 180 °C was studied by thermogravimetric analysis (TGA) in air up to 900 °C with a heating rate of 10 °C min⁻¹ using a Netzsch STA 409. FTIR spectra were recorded on a PerkinElmer spectrum 100 spectrometer in the range 650–4000 cm⁻¹. All the spectra were obtained using attenuated total reflectance accessory with a resolution of 2 cm⁻¹. Water absorption tests were performed using weight changes after and before soaking the membranes in deionized water at room temperature for 24 h. The water absorption (WA) was calculated by $WA (\%) = [(W_{wet} (g) - W_{dry} (g)) / W_{dry} (g)] 100$, where W_{wet} and W_{dry} are the weight of wetted and dried samples, respectively. The ionic exchange capacity (IEC) of the hybrid membrane was determined by acid-base titrations. The IEC was calculated according to $IEC = nH^+ / m_{dry}$, where IEC (mmol g⁻¹) is the number of millimoles of H⁺ (nH⁺) per dry weight of membrane (m_{dry}). Membranes were converted to H⁺ ionic form by immersion in HCl 1 N for 24 h. Afterwards, membranes were soaked in 50 ml of NaCl 1 M for another 24 h to produce the exchange of protons and sodium ions. Then, 50 ml of the solution was titrated with 0.005 M NaOH until equivalent point. Membranes were regenerated with 0.1 N HCl, washed with water and dried up to a constant weight using a vacuum oven at 80 °C. The conductivity of hybrid membranes was measured by electrochemical impedance spectroscopy (EIS) using a Gamry FAS2 Femtostat, Ag electrodes and a frequency range of 1–10⁵ Hz. The measurement was performed using a planar configuration, i.e. membranes are sandwiched between two silver electrodes. This configuration lets the evaluation of the conductivity across the membrane from one surface to the other. The measurements were conducted as a function of both relative humidity and temperature. The samples were allowed to equilibrate at the desired RH for 24 h inside a sealed chamber containing a saturated solution of NaNO₃ for the 62–70% range (for temperatures lower than 50 °C), 70–81% range (for temperature between 50 and 70 °C), 81–99% range (for temperatures between 70 and 90 °C) and water vapour for the 100% (for temperatures higher than 90 °C). Temperature and relative humidity have been measured using a Rotronic HYGROCLIP HK 25.

3. Results

The hybrid membranes are homogeneous, transparent, crack-free, and yellow coloured after the polymerization process at 60 °C. Thicknesses are included in the range between 700 and 200 μm. The thermal treatment at 110 or 180 °C does not affect the colour and transparency, although the membranes show a slightly loss of flexibility because of the sol-gel condensation reactions. Sulfonation process of membranes with HSO₃Cl solution damages partially the surface, while the sulfonation agent (CH₃)₃SiSO₃Cl does not produce any appreciable change. Fig. 2 shows a photograph of a hybrid membrane treated at 180 °C and sulfonated for 2 h with a high homogeneity. In this work, only the characterization of membranes sulfonated with (CH₃)₃SiSO₃Cl solution has been reported. Fig. 3 shows a FE-SEM photograph of a fractured surface of a membrane treated at 180 °C and sulfonated with (CH₃)₃SiSO₃Cl solution during 2 h. The figure shows a homogeneous material formed by nanosized agglomerates (25–50 nm) without degradation and phase separation, and a low size porosity (5–10 nm), very important to retention of water at high temperature. Micrographs of a hybrid membrane treated at 180 °C and sulfonated for 24 h are shown in Fig. 4. Morphology and topography of the membrane sulfonated for 24 h seems to be similar than that sulfonated for 2 h, however it can be observed that this sulfonation time is too high and membrane suffers a superficial degradation. EDX analyses of different hybrid particles have been performed, showing a high

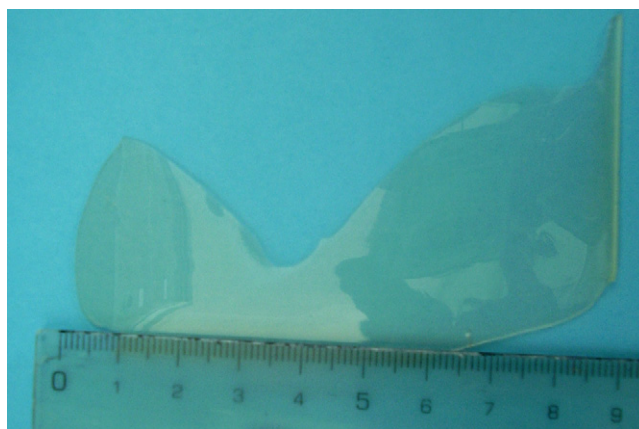


Fig. 2. Photograph of a hybrid membrane 20 TEOS-40 GPTMS-40 AP treated at 180 °C and sulfonated for 2 h.

homogeneity in the composition and the absence of phase separation. The EDX analysis does not reveal important variation of the elements concentration across the membrane surface.

TGA-DTA curves of membranes treated at 110 °C and sulfonated with (CH₃)₃SiSO₃Cl solution for 2 and 24 h are depicted in Fig. 5. Membranes treated at 180 °C present an analogous behaviour (not shown). Thermogravimetric curves show four regions. The first region, between room temperature and 200 °C, does not show any substantial change due to the membranes were treated previously at 110 °C, and desorption of physically absorbed water and residual solvents are almost complete. The second region, between 200 and 300 °C, presents an exothermic peak and an important weight loss of 9% and 15% for 2 and 24 h sulfonated membranes, respectively. These losses are assigned to the initial combustion of the organic components, mainly residual epoxy rings, pseudo-polyethylene oxide chains and decomposition of SO₃ groups [8,15]. The third region in TGA curves, between 300 and 500 °C, presents an important weight loss (40% and 46% for hybrid membranes sulfonated 2 and 24 h, respectively) and an exothermic peak assigned to the final decomposition of PEO chain. Above 500 °C, a broad exothermic peak (around 630 °C) and weight losses of 11% (2 h) and 8% (24 h) are observed. Both are assigned to the structure decomposition of organic components, mainly aromatic rings. The difference in weight loss between both membranes at the end of the test is not significant, although the smaller weight loss observed in the

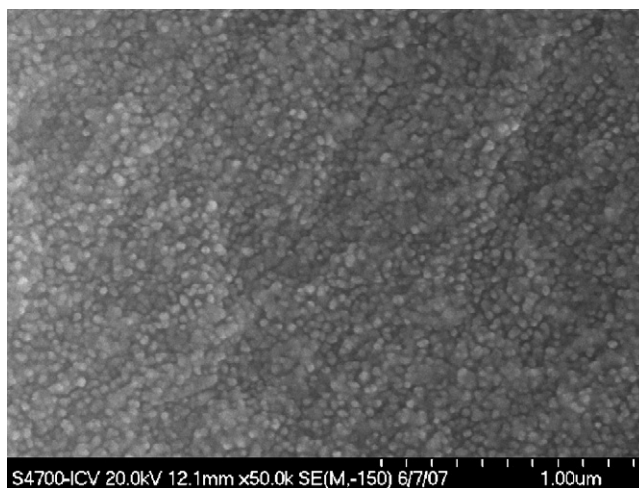


Fig. 3. FE-SEM photograph of a fractured surface of the hybrid membrane 20 TEOS-40 GPTMS-40 AP treated at 180 °C and sulfonated for 2 h.

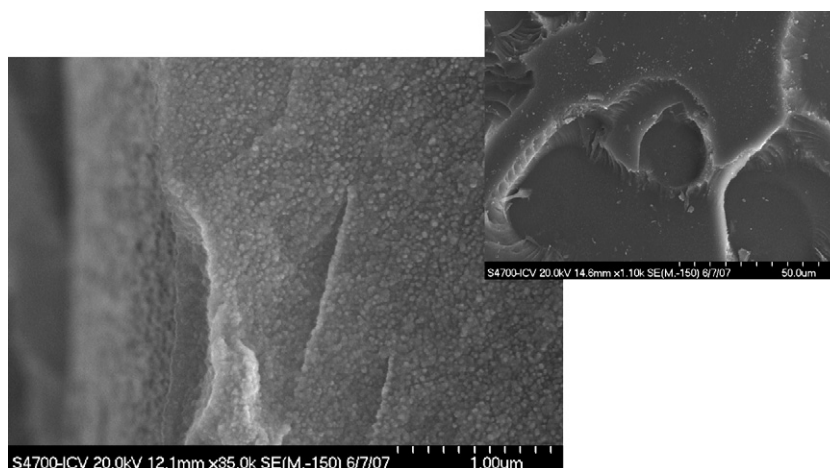


Fig. 4. FE-SEM photographs at different magnifications of a fractured surface of the hybrid membrane 20 TEOS–40 GPTMS–40 AP treated at 180 °C and sulfonated for 24 h.

membrane treated for 24 h could be associated with a higher consolidation of the inorganic structure, because of a longer treatment, and consequently a less amount of residual alkoxide groups that are eliminated during the TGA–DTA tests. The small weight loss observed up to 200 °C and the position of the lower temperature exothermic peak (beginning at 250 °C) indicate that the thermal stability of these hybrid membranes is enough for application in high temperature PEMFC.

Fig. 6 shows the FTIR absorbance spectra of sulfonated membranes at different thermal treatment, 110 and 180 °C, for 2 and 24 h in the 1750–650 cm^{-1} range. No significant changes in localization and intensity of spectra peaks can be observed, indicating that the hybrid structure is stable against thermal treatment and sulfonation processes. All the bands in the spectra are in good agreement with those coming from precursors and are assigned using literature data [5,16–20]. Bands related to aromatic ring of AP appear in the same region, between 1600 and 1400 cm^{-1} , than those related to GPTMS network. The sulfonic group incorporation was detected by FTIR due to the presence of a band at 1250 cm^{-1} , which was attributed to the S=O symmetric stretching vibration, and a characteristic band of the substituted benzene ring at 745 cm^{-1} . It is also observed a band at 680 cm^{-1} which is related to S–O bending vibration. The broad band at 1200–1000 cm^{-1} is due to oxide structure, obtained from reaction between TEOS and GPTMS where some of the vibrations modes of Si–O–Si overlap with those from di-substituted benzene rings and stretching bands of sulfonated groups.

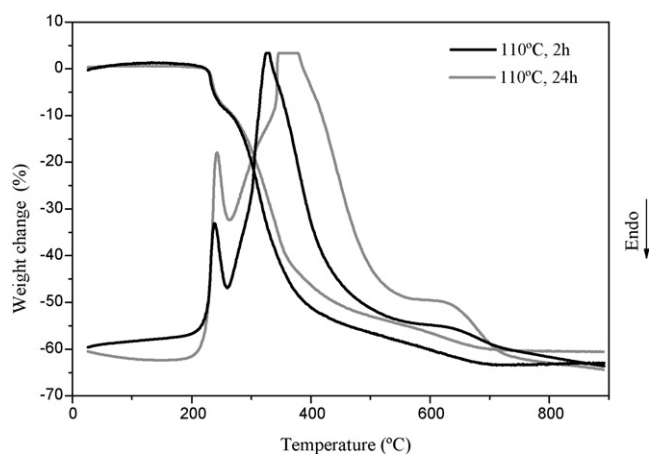


Fig. 5. TGA–DTA curves of hybrid membranes treated at 110 °C and sulfonated for different times.

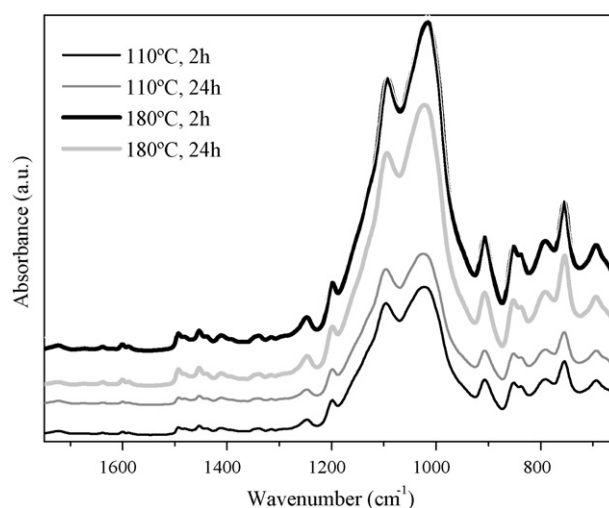


Fig. 6. FTIR spectra of hybrid membranes with different thermal treatments and sulfonation times.

Values of ion exchange capacity and water adsorption are shown in Table 1. Water uptake and IEC increase with the number of hydrophilic sulfonic acid groups attached to the hybrid chain. These parameters are crucial for proton conductivity through the formation of paths suitable for fast proton conduction. IEC values are quite close to each other, although the maximum value is obtained for the membrane treated at 180 °C and sulfonation for 24 h. Water uptakes between 13.4% and 17.1% were obtained for sulfonated hybrid membranes with maximum values for membranes treated at 180 °C. The increase of temperature produces a higher surface area (external area of porosity) due to condensation reactions that promotes loss of solvents and water producing additional porosity. The drying of sol–gel materials at low temperature (below 200 °C) produces this extension of the condensation reaction and removal of water and solvents from the gel system without a significant collapse of the gel structure (sintering), generating new low size

Table 1
Ion exchange capacity (IEC) and water adsorption of hybrid membranes.

Membrane	IEC (meq g^{-1})	Water uptake (%)
110 °C, 2 h	0.6	13.4
110 °C, 24 h	0.7	14.8
180 °C, 2 h	0.6	16.2
180 °C, 24 h	0.8	17.1

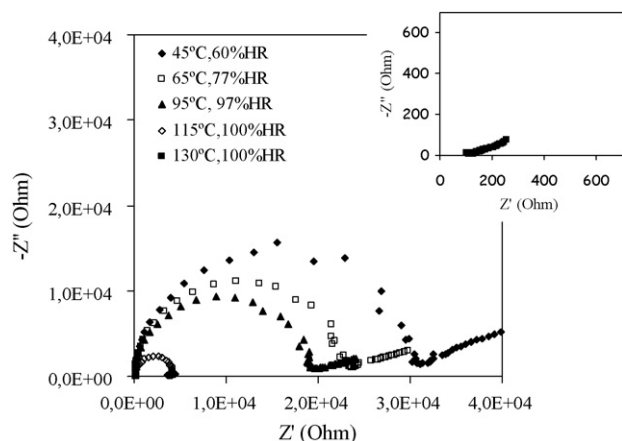


Fig. 7. Impedance spectra at different temperatures and relative humidity of a membrane treated at 110 °C and sulfonated for 2 h. The high frequency region is shown in an expanded view.

porosity (below 10 nm). It would be necessary higher temperatures to increase significantly the sintering of these materials with a remarkable reduction of porosity. The higher surface area of the membranes treated at 180 °C explains the greater water absorption.

All the complex impedance spectra (Nyquist plot) present a semicircle through the origin at high frequencies, and small inclined lines at low frequencies. As an example, Fig. 7 shows the impedance spectra of a membrane treated at 110 °C and sulfonated with $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ solution for 2 h. The semicircle can be represented with a typical equivalent circuit of a resistor and a capacitor connected in parallel corresponding to the bulk electrical properties, and the line a Warburg impedance originated by the diffusion process of protons. The conductivity σ of the samples in the transverse direction was calculated from the impedance data, using the relation $\sigma = t/RS$. In this equation t and S represent the thickness and electrode area of the sample, respectively. The resistance R was obtained from the intersection of the semicircle with the $\text{Re}(Z')$ axis calculated using fitting software. The presence of one time constant demonstrates the existence of a unique proton conduction mechanism based on water molecules as “vehicles” for the movement of protons across the membrane. The sulfonation process incorporates SO_3^- groups as new hopping points for protons reducing the free main distance among them. The consequence is a higher conductivity when the sulfonation degree increases. The rise of temperature and relative humidity generate a significant reduction of the semicircles, indicating a quickly decrease of the resistance that the membrane offers to the proton movement.

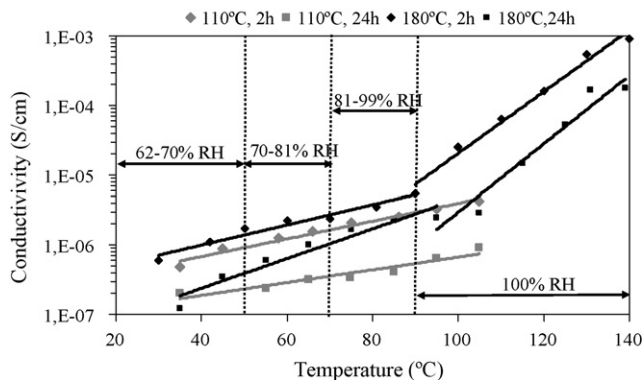


Fig. 8. Conductivity values as a function of temperature and relative humidity of hybrid membranes with different thermal treatments and sulfonation times.

Fig. 8 presents the conductivity values of the membranes as a function of temperature, relative humidity and sulfonation time. The general trend observed is the increase of conductivity with relative humidity and temperature because of proton conduction is a thermally activated process. Relative humidity defines the amount of water molecules occupying the porosity in the hybrid structure, enhancing the transport of protons through the material when it increases.

Two different thermal treatments were chosen to prove the role of water uptake in the proton conductivity. Membranes treated at 180 °C of temperature present an elevated surface area and a higher porosity due to the consolidation of the network. These membranes show an increase of conductivity above 100 °C due to the water retention and SO_3^- groups. Proton conductivity increases three orders of magnitude at a constant relative humidity of 100% when temperature changes from 100 to 140 °C, showing a limited dehydration.

For both thermal treatments, sulfonated membranes for 2 h present conductivities one order of magnitude higher than those sulfonated for 24 h. For example, the membrane with a thermal treatment of 180 °C and 24 h of sulfonation presents a value of $1.7 \times 10^{-4} \text{ S cm}^{-1}$ at 140 °C and 100% relative humidity compared with $1.3 \times 10^{-3} \text{ S cm}^{-1}$ for membranes sulfonated for 2 h. IEC and water uptake measurements do not show significant differences between both sulfonation times, meaning that the proton conductivity values should be comparable. Nevertheless, SEM studies (Fig. 4) show that membranes with sulfonation times of 24 h present a very superficial degradation. This partial damage in the structure affects to conduction paths, decreasing the proton conductivity. The proton conduction mechanism of sulfonated polymers is water assisted, and their hydration state is a crucial factor for a good electrochemical performance. Sulfonation process is a powerful process that can produce degradation when the degree of sulfonation is high, even through extensive sulfonation leads to water-soluble polymers. The degree of sulfonation can be controlled to exhibit a high ionic conductivity, good mechanical strength and a reasonably low affinity to methanol.

4. Conclusions

Organic–inorganic membranes using tetraethoxysilane (TEOS), 3-glycidoxypropyl trimethoxysilane, and 2-allylphenol have been synthesized by polymerization and inorganic sol–gel condensation. Sulfonation process was incorporated to the experimental procedure to provide proton conductivity. TGA–DTA curves show an excellent thermal stability up to 200 °C indicating that these hybrid membranes will be stable within temperature range of PEMFC application. SEM and proton conductivity confirm that 24 h of sulfonation is an elevated time and membranes suffer a partial degradation. The conductivity shows a general increase with temperature and relative humidity, reaching a maximum value of $1.3 \times 10^{-3} \text{ S cm}^{-1}$ at 140 °C and 100% RH.

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