Properties of Polystyrene/Acrylic Acid Membranes After Sulphonation Reactions

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Abstract: *Sulphonation reaction in styrenic membranes is a common method used to graft ionic groups needed to enhance proton conductivity in polymeric electrolytes (PEM). A synthesized copolymer of styrene and acrylic acid (94/6 % mol) was partially crosslinked using a trifunctional monomer, trimethylolpropane trimethacrylate (TMPTMA) (0.01% mol), like a crosslinking agent. The obtained material was subjected to different sulphonation reactions in order to prepare several PEM membranes. The sulphonation reactions used sulphuric acid (H₂SO₄, 98%) at 50, 75 and 100 %molar ratio considering amount of styrene rings, during 1 and 2 hours of reaction time. Fourier transformed infrared spectroscopy (FTIR) spectra were obtained to identify specific chemical groups in these materials. Thermogravimetric analysis (TGA) and Dynamic Mechanical Analysis (DMA) were used to evaluate the thermal stability and mechanical effects after sulphonation reactions. Water absorption and its effect on proton conductivity by means of Electrochemical Impedance Spectroscopy (EIS) were also evaluated. FTIR spectra show characteristic bands corresponding to sulphone groups within macromolecular structure. Sulphonating agent concentration and/or sulphonation time induce higher glass transition temperatures and no changes in thermal stability when comparing with the no sulphonated material. Latter condition also allows higher water absorption and an enhancement in proton conductivity.*

1. INTRODUCTION

Perfluorosulphonic acid membranes (Nafion) are the most convenient films to use into a PEMFC nowadays, basically due to the ion activity of the sulphonic groups. According to the latter, there is a search for cheaper polymeric materials treated with sulphonation reactions, to graft such groups and increase their ionic activity, to be able to use them as polyelectrolytes into a fuel cell. Alternative membranes can be divided in 3 groups: modified perfluorosulphonic acid membranes, acid-base complex membranes and sulphonated alternated hydrocarbon polymers. The last group involves several systems as well as preparation methods; it is also usually of very low cost with an important variety of common materials to find. They also have high water absorption in a wide temperature range and easy to recycle [1].

Such membranes can be prepared by polymerization or copolymerization reactions of monomers containing anionic or cationic radicals; otherwise such radicals can be introduced into the poly-

mer through chemical reactions or by functional group grafting reactions. For the latter, sulphonation reactions is one of the most common methods, where for the case of polystyrene, an aromatic electrophilic substitution is carried out and a hydrogen atom is changed by a sulphonic acid group [1-3].

A research group [3] studied the mechanical behavior and ionic conductivity of a sulphonated poly(aryletherketone) bifenilate at several sulphonation times. They found excellent mechanical properties, high dimensional stability and ionic conductivity for a degree of sulphonation of the unity (DS=1) for a reaction time of 3 hours and evaluated at 80 ºC. On the other hand, Sherazi et al [4] crosslinked UHMWPE with styrene and prepared membranes by press molding to then sulphonate them with chlorosulphonic acid. They obtained membranes with high proton conductivity and lower permeability to methanol than Nafion.

Another easy two-step method with lower cost is the copolymerization of styrene-divinyl benzene and further sulphonation reaction with concentrated sulphuric acid [5]. Moreover, Deb and Mathew [6] reported the characteristics of sulphonated styrene-acrylic acid copolymers; they experimented with styrene levels of

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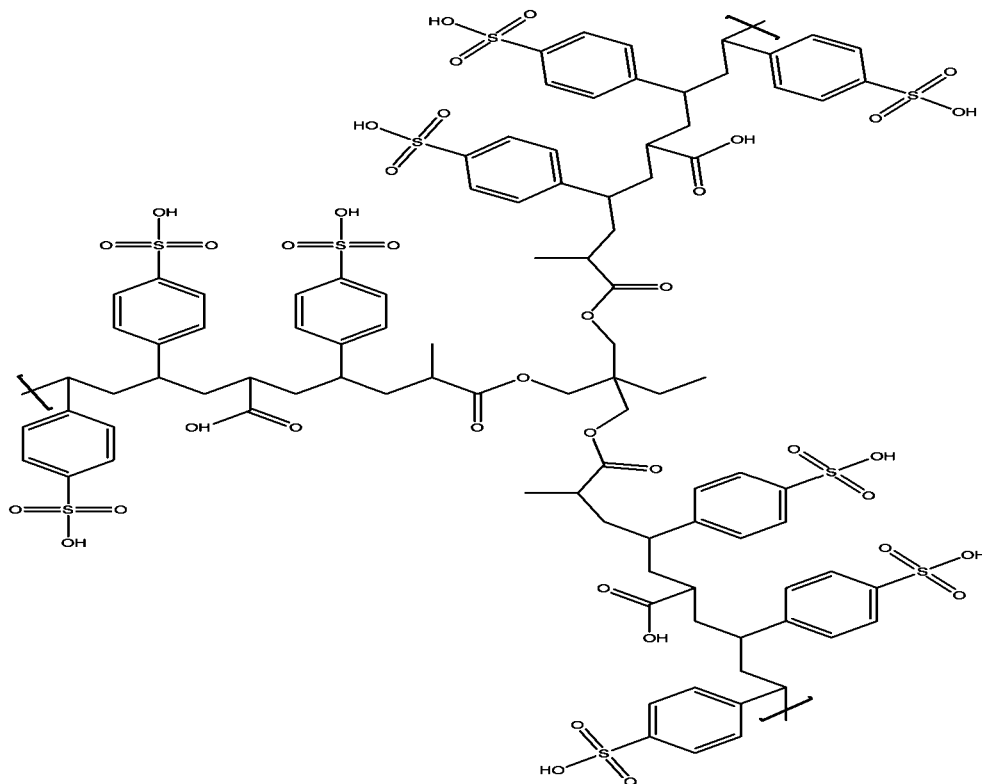Phone: +52(844)438 9830 xt.1322, fax (844)438 9839

Figure 1. Proposed structure for the sulphonated copolymer.

47-55 % mol. According with their results, such materials are useful as pH sensors as well.

Paula et al [7] reported the synthesis of different molar ratios of poly(styrene-acrylic acid) copolymers through radical polymerization at 110 ºC during 2 hours and then sulphonated at 40 ºC during 90 minutes. The 92:8 molar ratio copolymer showed high conductivity values for different moisture content.

Our research group has been preparing copolymers of styrene and acrylic acid at different ratios and different levels of crosslinking with a tri-functional agent (TMPTMA) to enhance mechanical properties [8]; however, sulphonation procedure is a basic step to control during membrane preparation, since such chemical groups will define the ionic conduction properties of the final material.

2. EXPERIMENTAL

2.1. Synthesis of Crosslinked Copolymers

Monomers were carefully distilled previous to the synthesis reaction. The radical copolymerization was carried out in a 100 mL glass reactor loaded with styrene and acrylic acid in a 94:6 molar ratio and benzoyl peroxide 0.05% mol as initiator. After the initiator addition, the crosslinking agent (TMPTMA - 0.01% mol), previously dissolved in styrene, was added in drops at time intervals of 2 min. The reactor was kept under nitrogen atmosphere at 100 ºC and mechanical stirring (250 rpm) during 2 hours. The copolymer sinthezised was dissolved in acetone and the solution precipitated into methanol; the latter procedure was repeated twice in order to eliminate low molecular weight material and the solid left to dry overnight and then into a vacuum oven. The percent of copolymeri-

zation yield, calculated by gravimetric measurements, reached 38%.

2.2. Sulphonation of copolymers

The copolymer was sulphonated in a similar reactor used for the synthesis. About 2 g of the copolymer was dissolved in 30 mL of dichloromethane at room temperature using mechanical stirring (250 rpm). Once the material dissolved completely, the system was heated to 40 ºC before the sulphuric acid addition. The amount of aromatic rings in the copolymer was calculated and the acid added to graft 50, 75 and 100 %mol of such rings. Sulphonation reaction time was controlled to have 1 and 2 hours and ended by adding 100 mL of cold distilled water (kept previously into an ice bath). Expected crosslinked and sulphonated copolymer chemical structure is shown in Figure 1.

2.3. Characterization of Copolymers

An aliquot of each copolymer (0.02 g) was dissolved with THF (1 ml) and the solution deposited in a flat confined glass plate in order to have films of approximately 0.03 mm thickness after solvent evaporation (casting). FTIR spectra of the films were recorded using a Nicolet Avatar 330 instrument with 64 scans and a resolution of 4 cm^{-1}.

TGA thermograms were carried out in a Q500 TA Instruments apparatus. Approximately 20 mg of sample was placed into the thermobalance and evaluated from ambient temperature up to 700 ºC, with a 10 ºC/min thermal ramp under nitrogen atmosphere. Mass loss was recorded along temperature.

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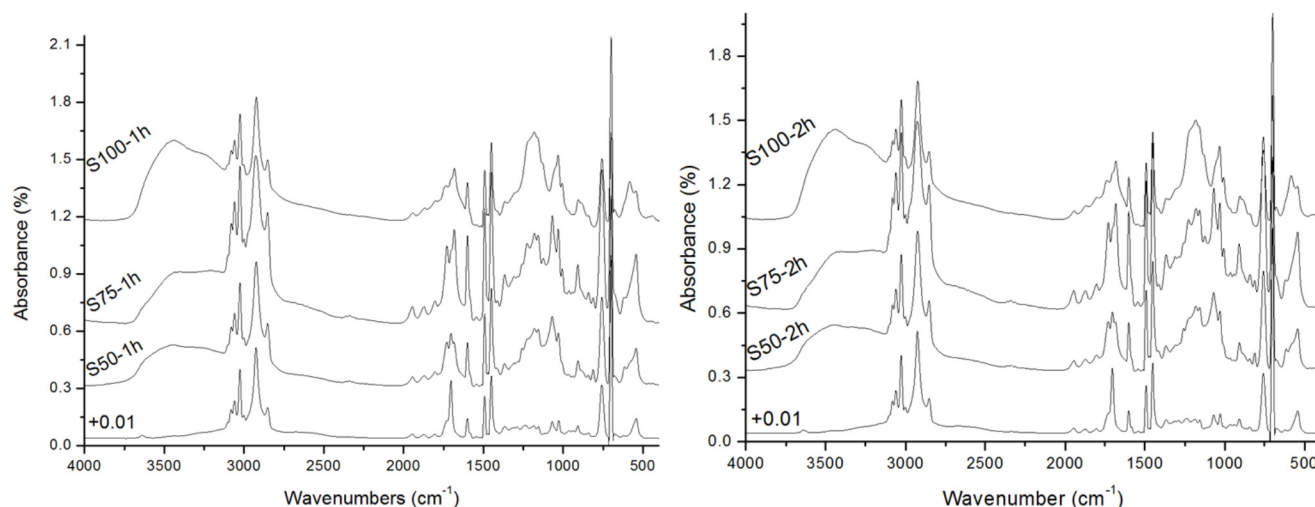*/ J. New Mat. Electrochem. Systems*

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Figure 2. FTIR spectra of copolymer sulphonated at 50, 75 and 100 % mol at 2 reaction times (1 and 2 hours).
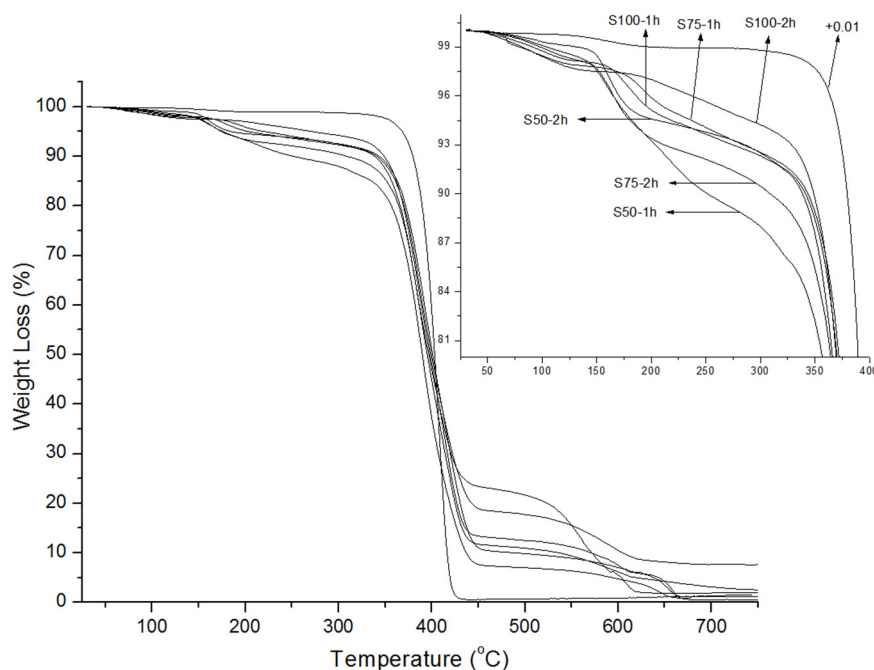

Figure 3. TGA thermograms for sulphonated copolymers.

Viscoelastic properties were also evaluated by means of a DMA TA Instruments Q800. A tension accessory was used for deformation, with amplitude of 20 microns and a frequency of 1 Hz in the temperature range of ambient to 130 °C and a ramp of 5 °C/min.

Capacity of water absorption was obtained gravimetrically obtaining their dry weight initially and after 24 hours of being immersed into a 0.05 M H_2SO_4 solution, washed thoroughly with ultra pure water and immersed again in same type of water.

Ionic conductivity of sulphonated copolymers was obtained with a potentiostat/galvanostat BioLogic SP-300, using the EIS technique. The potentiostat mode was used in the frequency range of 2 to 30 mHz at the open circuit potential, collecting 10 points by decade. Measurements were carried out with a two-electrode system with a platinum sheet as the electrode supporting the membrane in one side and a hole full of mercury with a platinum wire (electrical contact) in the other side.

3. RESULTS AND DISCUSSION

FTIR is a very useful technique to evaluate the addition of sulphonic groups into the copolymer. Figure 2 shows the spectra for the cross-linked material with 0.01 % TMPTMA and sulphonated at different levels and time.

Many important differences can be seen between non and sulphonated copolymer, the most noticeable is the formation trend of a wide and strong band at 3500-3100 cm^{-1}. Such band is a direct indication of the SO_3H group addition, since it corresponds to the absorption of the OH from the sulphonic group. A similar band formation was also reported by Proença [9] for membranes of sulphonated polystyrene and polyaniline.

Another spectra region showing differences after sulphonation is found at 1400-1000 cm^{-1}, corresponding to the SO_2 asymmetric stretching (1390-1290 and 1182 cm^{-1}) and for the symmetric stretching bands (1190-1120 and 1029 cm^{-1}). Such signals define the addition of sulphonic groups. The wide band at 1182 cm^{-1} observed for the 100 %mol at 1 and 2 hours of reaction time indicate that for higher amount of sulphuric acid there is more sulphonation reaction effectively happening in the copolymer [10]. Proença [9] also observed such changes in the sulphonated styrene and Acosta [11] for the rising band at 1005 cm^{-1} when sulphonating poly(styrene-butadiene) copolymers.

Thermogravimetric analysis was also carried out in order to evaluate thermal stability for sulphonated copolymers. Figure 3 shows the weight loss curves for the materials. It is easy to note that non
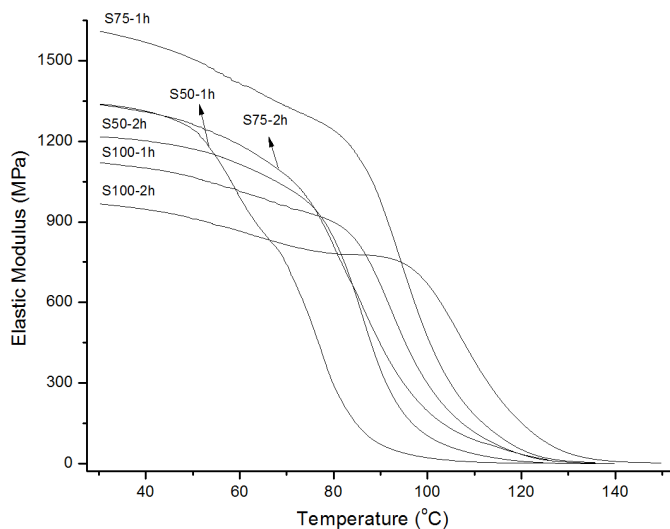
Figure 4. Elastic modulus (E´) for non and sulphonated copolymers.

Figure 5. Viscous modulus (E´´) for non and sulphonated copolymers.

Figure 6. Water absorption for sulphonated samples.

sulphonated material (+0.01) is the most thermally stable, showing basically one decomposition step at around 350 ºC without leaving residues. On the other hand, sulphonated materials decompose in several steps. The first step (50-140 ºC), is basically associated with water loss, which is in the material due to the hydrophilic characteristic induced by the sulphonic groups; it actually follows a tendency of more mass loss with higher sulphonating agent used to prepare them. A second step (150-350 ºC) is associated to de-sulphonation reactions with a tendency to stabilize with higher level of sulphonation, as reported previously by other authors [12, 13]. The third and main step is due to the copolymer backbone decomposition (350-450 ºC). Finally, the fourth step is related to the level of residues left for each material, which is difficult to associate to a specific reaction, but in our case are showing fewer residues for lower level of sulphonation.

Dynamic Mechanical Analysis was carried out to follow the viscoelastic property changes throughout sulphonation. Figure 4 shows the elastic modulus traces for the materials. The most important observation is that all sulphonated copolymers have higher elastic modulus values (E´) at room temperature than non-sulphonated material. This is a consequence of some crosslinking reactions or strong interactions (hydrogen bridges) among sulphonic groups grafted to the main structure. On the other hand, when comparing among sulphonated materials, it is possible to see a tendency to reduce E' values at room temperature, specifically when higher and longer sulphonation reaction conditions are used. This effect should be related to the adsorbed water into the polymeric structure, which works like a plasticizer and is difficult to eliminate due to the higher hydrophilicity conferred by the sulphonic groups. The latter behaves according to TGA first step weight loss due to water loss. Finally, if the main loss of the TGA curve is considered as the decomposition temperature, there is a very similar behavior for all materials; it means that sulphonation reactions are not reducing the thermal stability of the copolymer.

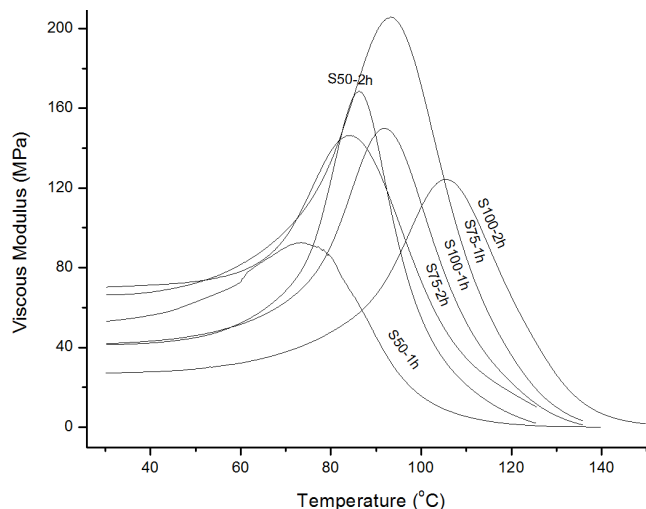Figure 5 shows the viscous modulii for the same samples ob-

served in the figure 4. Same tendency is observed in Tg values, if the peak maxima are considered as the thermal transition, in full consistency with E´ results, where higher concentration of sulphonating agent and longer reaction times enhance the thermal transition due to reduced molecular mobility, as a comsequence of strong internal interactions.
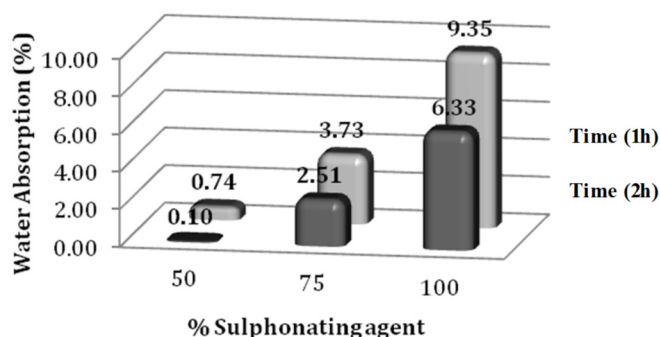
Considering that water absorption in the materials play an important role, measurements were carried out to inter-compare the copolymers through the sulphonation conditions and Figure 6 shows the results obtained. It is very easy to notice that for the higher amount of sulphonating agent and the longer reaction time the absorption of water is enhanced, in agreement with previous results where a water intake was detected and reflected the results discussed. According to sulphonation conditions, sulphonic groups graft into de main copolymer structure, enhancing hydrophilicity and changing their thermal and mechanical characteristics. Several authors have observed similar effect of sulphonic groups for polymer materials [14, 15].

The electrochemical behavior of sulphonated copolymers was evaluated by Electrochemical Impedance Spectroscopy (EIS) and compared with Nafion 117. The impedance spectra (Nyquist), sim-

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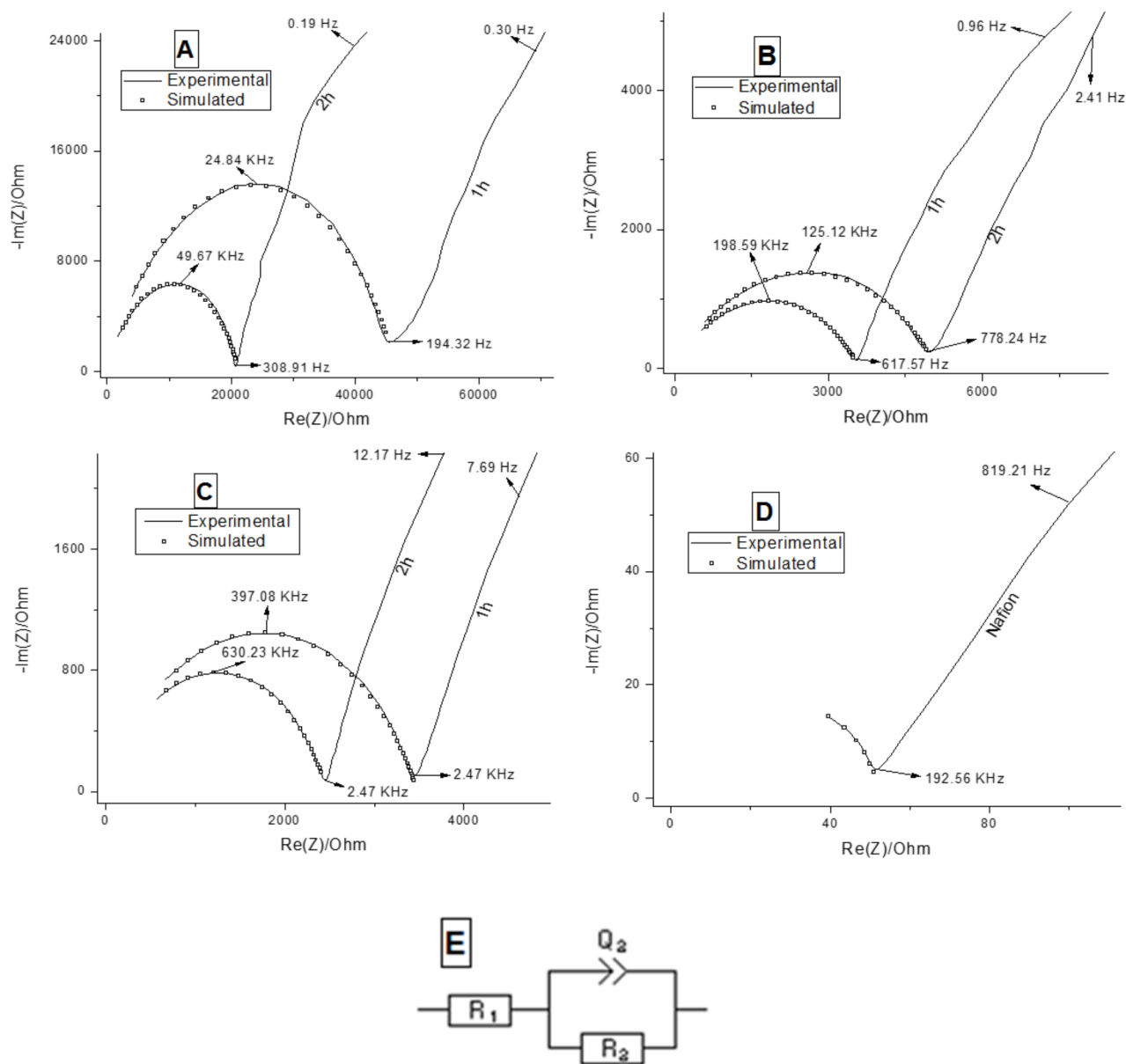/ J. New Mat. Electrochem. Systems

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Figure 7. EIS spectra for sulphonated copolymers at: A= 50, B= 75 and C= 100 % mol and compared with Nafion (D). Equivalent circuit for adjusted curves (E).

ulated curves and the equivalent circuit are shown in Figure 7.

The Nyquist impedance spectra involve the real (Re(Z)) and imaginary (Im(Z)) axes and their data is only adjusted or simulated in high frequency region (semi-circle), since lower frequencies describe diffusion and other phenomena out of our interest. From simulated curves several electrochemical parameters were obtained: ohmic resistance from the membrane (R_1), constant phase element (Q_2) and resistance to charge transfer ($R\infty$). Such parameters are useful to compare materials and from R_1 the proton conductivity (σ, with S/cm units) can be calculated through the Ho equation [16]:

$$\sigma = eR_1A$$

where "e" is membrane thickness and "A" area of transversal

section. In our experiments the hole containing mercury electrode is 0.45 cm^2. Figure 8 shows the proton conductivity obtained for sulphonated materials. A very clear tendency to enhanced proton conductivity values is seen for copolymers treated with higher amount of sulphonating agent at longer time, noticing that copolymer with 100 % mol sulphonation, even during 1 hour, have higher values than Nafion. Such values are in direct proportion to ohmic resistance (R_1), which in turn has the most influence to ohmic resistance of a fuel cell.

Proton conductivity values (ohmic resistance) have an important effect in the membrane polarization curves, which in turn are very useful to determine fuel cell performance. It is also directly related to absorbed water in the membrane, since proton conduction occurs by diffusion through the water inside hydrated clusters.
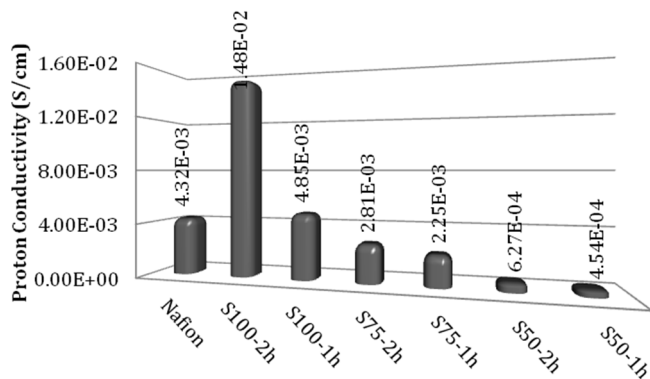
Figure 8. Proton conductivity (s) for sulphonated copolymers and Nafion 117.

4. CONCLUSIONS

Evaluation of sulphonated copolymers of crosslinked poly(styrene-co-acrylic acid) indicated that presence of sulphonic groups which induce increment in Tg values, higher elastic modulus and similar thermal stability comparing with non sulphonated copolymer. The higher amount of sulphonating agent and longer times of sulphonation reaction reduce slightly such high elastic modulus as a consequence of higher water absorption, but enhance proton conductivity. The most sulphonated membrane, by concentration of agent and longer reaction time (S100-2h), had a distinguished performance, since even with less ability to absorb water obtain higher level of proton conductivity when comparing with Nafion.

5. ACKNOWLEDGMENTS

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