

# DGEBA/PVPh-HEM Semi-IPN for use as proton conductive membranes.

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Research on renewable and less-polluting energy sources became essential for the development and sustainable use of natural resources. Devices such as fuel cells (FC) are pointed as an environmentally attractive alternative to conventional energy sources. The increasing demand for new energy conversion technologies compatible with the current scenario lead the study of FC one of the most promising research areas nowadays [1]. In order to decrease its cost, the FC efficiency must be increased, being of key importance to develop optimized conductive polymer membranes. The development of semi-IPN (SIPN) membranes for FC application has been proposed based on their chemical and mechanical stability, as well as other enhanced properties, compared to conventional polymer membranes. The IUPAC definition of a SIPN is "A polymer comprising one or more networks and one or more linear or branched polymer(s) characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules." Depending on the solubility of the non-crosslinked polymer, the membrane based on a SIPN can have high chemical stability against oxidation processes.

The main goal of the present work is the synthesis and characterization of a SIPN and a sulfonated SIPN to be used as proton conductive membranes. The crosslinked polymer matrices were obtained from curing reactions between the diglycidyl ether of bisphenol A (DGEBA) and poly (4-vinylphenol-*co*-2-hydroxyethyl methacrylate) (PVPh-HEM) in the presence of the curing agent 4,4-diaminodiphenyl sulfone (DDS). Different DGEBA/PVPh-HEM weight ratios were used, varying the concentration of PVPh-HEM films between 9 and 50%, keeping the molar ratio of DGEBA:DDS as 1:1. The solutions were deposited on Petry dishes and membranes were obtained after complete evaporation of the solvent. The membrane with the best properties, 50% PVPh-HEM, were sulfonated in 0.25:1, 0.5:1, 1:1 and 2:1 styrene:sulfonic acid ratio. The SIPN samples were characterized by FTIR, DSC and Thermogravimetric Analyses (TG). The 50% PVPh-HEM membrane was immersed in 5% H<sub>3</sub>PO<sub>4</sub> solution at room temperature for 24 hour and it was characterized by Electron Spectroscopy Impedance (EIS). All the sulfonated membranes were characterized by FTIR and the 0.25:1 was immersed in deionized water at room temperature for 24 hours to be characterized by EIS.

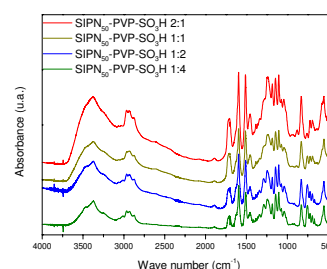
For membranes containing between 40 and 50% PVPh-HEM, vibrational infrared spectroscopy (FTIR) evidenced the DGEBA epoxy ring opening reaction, indicated by the disappearance of the 916 cm<sup>-1</sup> band. Other compositions showed variation in the intensity of this band, indicating that only a certain number of epoxy rings undergo the opening reaction.

All membranes obtained were analyzed by TG and

showed early degradation above 300 °C. It was observed the presence of an unique T<sub>g</sub> above 120 °C for all samples. A T<sub>g</sub> increase with the PVPh-HEM composition was observed, indicating the existence of nanostructures between 20-40nm in the system. No other thermal event was observed at temperatures between -25 and 300 °C, indicating that the system does not undergo phase changes at this temperature range.

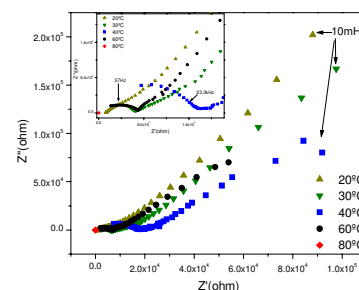
The 50% PVPh-HEM EIS analysis allowed calculating the conductivity of this membrane around 10<sup>-7</sup>S.cm<sup>-1</sup>.

Infrared spectroscopy (FTIR) evidenced the sulfonation of aromatic groups by the appearance of the 1240 cm<sup>-1</sup> band, as shown in the Figure 1:



**Figure 1:** FTIR spectra of samples SIPN-PVPh-HEM 0.25:1, 0.5:1, 1:1 and 2:1 styrene:sulfonic acid.

The 50% SIPN-PVPh-HEM5%H<sub>3</sub>PO<sub>4</sub> membrane EIS analysis shows conductivity values around 10<sup>-7</sup>S.cm<sup>-1</sup>. Considering the low conductivity values of the 50% SIPN-PVPh-HEM5%H<sub>3</sub>PO<sub>4</sub>, a same composition membrane was sulfonated and characterized by EIS. Figure 2 shows the EIS spectrum for the 50% SIPN-PVPh-HEM-SO<sub>3</sub>H (0.25:1) and the Table 1 shows the conductivity values obtained.



**Figure 2:** SIPN 50% PVPh-HEM-SO<sub>3</sub>H (0.25:1) membrane EIS spectra.

**Table 1:** Conductivity values as a function of temperature

Temperature	20 °C	30 °C	40 °C	60 °C
$\sigma$ (S.cm <sup>-1</sup> )	(8,35 × 10 <sup>-4</sup> ) ± 2,20 × 10 <sup>-5</sup>	(6,1 × 10 <sup>-4</sup> ) ± 1,56 × 10 <sup>-5</sup>	(2,84 × 10 <sup>-4</sup> ) ± 2,23 × 10 <sup>-5</sup>	(3,79 × 10 <sup>-5</sup> ) ± 5,27 × 10 <sup>-6</sup>

The conductivity values observed for the sulfonated membrane was about 10<sup>-4</sup>S.cm<sup>-1</sup> between 20°C and 40°C and 10<sup>-5</sup>S.cm<sup>-1</sup>. The conductivity decrease was attributed to the membrane mechanical stability loss at the 100% relative humidity environment used for the measures. The experimental environment is being changed to avoid the continuum water absorption during the measurements at increasing temperature.

[1] Silveira J.L. *et al.* Renewable Energy and Sustainable Reviews 13, 2525, 2009.

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