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Polyacrylonitrile-based sulfonated membranes: synthesis and thermal analysis

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Abstract – In the present work, preparation and characterization of sulfonated ABS membranes are reported. Sulfonated membranes were characterized by thermal analysis techniques, which evidenced the thermal stability up to 370 °C and indicated the formation of nanodomains associated to sulfonic acid-water supramolecular structures, represented by [-$SO_3H(H_2O)_n$].

Fuel Cells (FC) are currently being pointed as the most promising conversion devices to be used as power sources in mobile, vehicular and stationary applications, in substitution to conventional energy sources. Most of the prototypes and commercial devices developed until now use Nafion as the proton conduction membrane [1], however, several issues on stability and conductivity at high temperatures (above 100 °C) are reported and considered as limiting characteristics of the Nafion membranes. Different approaches are reported in the literature, from nanocomposites to sulfonation of commercial polymers [2], aiming to develop proton conductive membranes with enhanced properties. In the present work, the properties of a proton conductive membrane based on poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) obtained by sulfonation are described.

The procedure employed for sulfonation was adapted from Elabd and co-workers [3] and the ratios of sulfonating agent to the styrene units used were 1:4, 1:2, 1:1 and 2:1. After the reaction time, the polymers were washed with distilled water and dried under vacuum. Samples were characterized by Thermogravimmetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Infrared Spectroscopy (FTIR) and Impedance Spectroscopy (EIS).

TGA curves showed that thermal decomposition temperature (near 370 °C for pure ABS) is almost unchanged with the sulfonation degree. Additionally, a mass loss increase was detected with the sulfonating degree up to 370 °C, associated to the residual water elimination from the membranes. ABS-SO_3H membranes exhibited two glass transition temperatures, one between 50 and 60 °C and other near 109-112 °C. This behavior indicates a structural ordering up to a hundred nanometers involving sulfonic acid groups and water molecules, which can be represented by [-$SO_3H(H_2O)_n$] and which possesses a lower T_g value than the main polymer chain. Sulfonic acid membranes, such as Nafion, exhibit two glass transition temperatures (T_g) under hydration conditions. These different T_g values are related to supramolecular structures with different organization degrees, interaction forces and, consequently, molecular mobilities. According to Eisenberg and co-workers [4], these thermal events correspond to two glass transitions: one of the perfluorocarbon main chain and other of the ionic hydrated domains. The presence of nanometer size ordered structures in ABS-SO_3H membranes can contribute to the proton transport due to the connection among these hydrated nanodomains, which allows the ion conduction in the membrane.

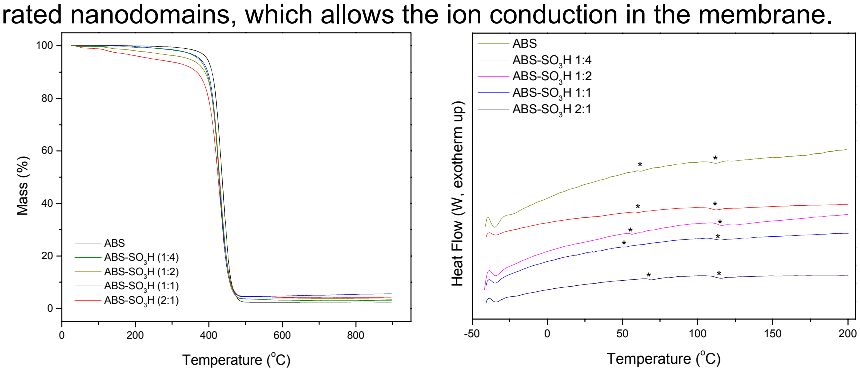

Figure 1. TGA (a) and DSC (b) curves for ABS-SO_3H membranes.

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CNPq, FAPERJ, Rede de Células a Combustível do tipo PEM.