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Morphological Investigation of Nafion and Nafion-SiO_2 hybrid membranes by SAXS analysis in dry and wet environments.

M. A. Dresch(1)* B.R. Matos(1), F.C. Fonseca(1), M. Linardi(1), J.F.Q. Rey(2) and E.I. Santiago(1)

(1) Instituto de Pesquisas Energéticas e Nucleares, São Paulo, 05508-000, Brazil.
(2) Universidade Federal do ABC, Santo André, 09210170, Brazil.
* Corresponding author: e-mail: madresch@ipen.br

Abstract – Nafion-SiO_2 hybrid membranes were prepared by the incorporation of SiO_2 into commercial Nafion 115 for applications as electrolytes in proton exchange membrane fuel cells (PEMFC) operating at high temperature (~130ºC). These hybrids were produced by conventional *in-situ* sol-gel method using Tetraethyl Ortosilicate (TEOS) as the silicon precursor, and some synthesis parameters, such as the nature of alcohol (methanol, ethanol, and 2-propanol) used as solvent in the sol-gel reaction were evaluated. The morphological changes in polymeric matrix were analyzed by water-uptake and small angle X-ray scattering measurements (SAXS). These hybrids were tested in single cells by polarization curves at high temperature.

Hybrid electrolytes based of Nafion-SiO_2 for PEM fuel cell operating at high temperature have been considered promising materials owing to higher proton conductivity compared to the unfilled polymer[1]. In this study, Nafion-SiO_2 electrolyte membranes were prepared by in-situ incorporation of inorganic particles into commercial Nafion membranes (115, DuPont) by means of conventional sol-gel procedure. Primarily the membrane was previously dried to determine the initial weight. The sol-gel reactions occurred after the immersion of Nafion membranes in different alcoholic media (methanol, ethanol, or 2-propanol) with subsequent addition of the silica precursor (TEOS). Afterwards, the acid catalyst was added to promote the hydrolysis reaction of the TEOS, followed by the drying of the samples at 100ºC. The degree of the incorporation of silica and the water retention capacity of the hybrids were determinate by gravimetry. The data indicate that silica content is dependent on the alcohol employed in sol-gel reactions. The water retention in hybrids is larger than that observed to unmodified Nafion. Hybrids synthesized in ethanol media presents 45% of water uptake, which is 55% superior of unmodified Nafion.

Small angle X-ray scattering measurements (SAXS) were performed in order to evaluate the morphological changes of the hybrids prepared by different sol-gel environments in dry and wet conditions. The Figure 1 shows the SAXS curves for Nafion-SiO_2 hybrids and unmodified Nafion membranes in dried state. A correlation length scattering maximum is observed and the values of *q* is not changed significantly[2]. Such evidences indicate that ionic clusters network was not modified by the presence of the inorganic nanoparticles. In wet state a shift of correlation length is observed, when compared to dried state membranes as shown in Figure 2. The water incorporation changes the distance between ionic group centers. The SAXS curves for hybrids show that the shift of the scattering maximum is larger in comparison to unmodified Nafion, indicating that the presence of silica allowed a higher water uptake, in good accordance with gravimetric results and single fuel cell tests.

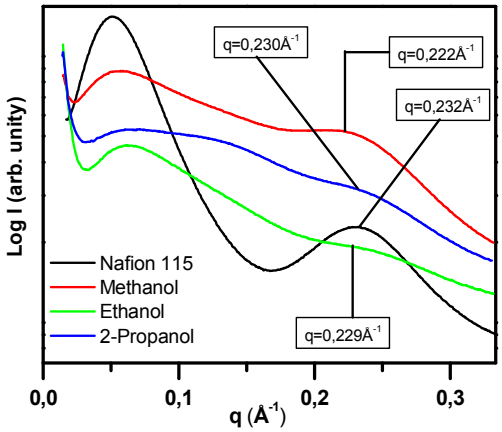

FIGURE 1: Small-angle X-ray scattering in dried state for Nafion and Nafion-SiO_2 hybrids synthesized in different environments

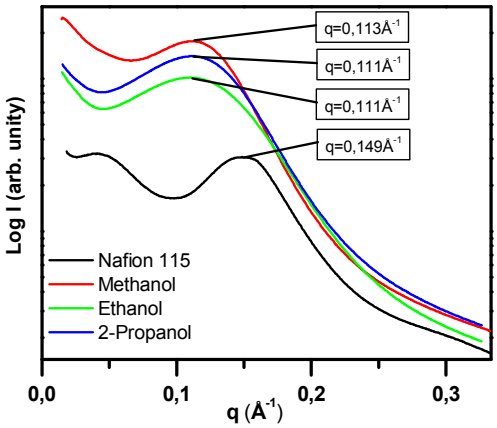

FIGURE 2: Small-angle X-ray scattering in wet state for Nafion and Nafion-SiO_2 hybrids synthesized in different environments

References

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