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Hybrid Proton Conducting Membrane Based on SPEEK and Modified Silica

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Abstract – The objective of this research is to develop a new type of ion exchange membrane, which based on sulfonated PEEK (SPEEK) with differents types of modified silicas. The influence of phosphotungstic acid (HPW) immobilized in the silica matrix (8.3% and 16.0% of HPW) and the influence of sulfonic group attached in silica matrix (4.2% and 9.0% total sulfur) were evaluated on proton conductivity, water uptake of membranes SPEEKs with different sulfonated degree were obtained by the latter method. The influence of modified silicas on the forming of the ion domain of SPEEK was studied by SAXS and H NMR measurement.

To overcome drawbacks such as instability to ethanol and high alcohol permeability, due to the affinity of alcohol to the sulfonic groups, composite membranes compounded by sulfonated polymers and modified silica have been proposed for direct methanol fuel cell [1].Proton conducting nanocomposites membranes consisting on SPEEK matrix (sulfonation degree=43%) where modified silica has been incorporated *ex-situ* by sol-gel process have been prepared.

Results show that water uptake decreases with loading of silica functionalized, while the opposite is observed by increasing contents of silica unmodified (Fig.1). The best conductivity (49.80mS/cm) at room temperature was obtained for membranes containing silica (4% wt) modified with 9% of SO_3H (the percentage being related to total sulfur) (Table 1). This value is better than obtained for SPEEK containing unmodified silica but lower than the one of pure SPEEK of same sulfonation degree. The study of the nanostructural features of the membranes performed by SAXS (Small-Angle X-Ray Scattering) allowed to explain the water uptake behavior, evidencing that this property increases with the number of nanometric SO_3H-rich hydrophilic domains dispersed in the matrix and that incorporation of silica modified with HPW impedes the domains formation. The conductivity of the samples also depends of nanostructure and is promoted by the increase on connectivity between the hydrophilic nanodomains. Preliminary H NMR measurements show that the diffusion coefficients of protons in the membranes are much lower than in pure water and that they present a decrease with the diffusion time typical of diffusion mechanism in confined medium. The first results allow to estimate the average limit corresponding to an homogeneous diffusion around 10 micrometers.

Table 1: Proton conductivity at 80ºC of hybrids membranes

Samples	Proton conctivity (mS/cm)
SPEEK	96.34
SPEEK+4%SiO_2SO_3H9%	49.80
SPEEK+4%SiO_2SO_3H4%	18.94
SPEEK+4%SiO_2HPW16%	43.31
SPEEK+4%SiO_2HPW16%	27.54
SPEEK+4%SiO_2	21.21

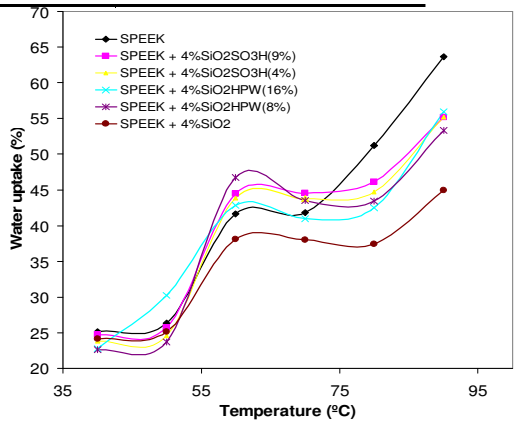

Figure 1: Water uptake of hybrids membranes

References

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