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New hybrid proton conducting zirconium oxide-SPEEK membranes for direct ethanol fuel cell

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Abstract – Hybrid zirconia-SPEEK proton conducting membranes for direct ethanol fuel cells have been prepared. For ZrO_2-containing membranes without phosphotungstic acid (HPW), water sorption is similar to pure SPEEK ones, while incorporation of HPW drastically increases water sorption. For all membranes containing zirconia ethanol permeability is reduced resulting on an increase of barriers properties. Membranes performance is related to nanostructural features investigated by SAXS.

In recent works, organic-inorganic composites membranes have been prepared for use in direct alcohols fuel cells (DAFCs), aiming to improve water retention and to increase the proton conductivity compared to pure polymer based ones. Since inorganic oxides are impermeable to ethanol, their incorporation in a polymeric matrix usually increases the barrier property of the resulting membrane [1]. Phosphotungstic acid (HPW) has been described in the literature as a good proton conductor, but the main disadvantage of its use in membranes is its high solubility in water. To overcome this problem, the *in situ* generation of an inorganic oxide network from hydrolysis and condensation of a metallic alkoxide is proposed. In this work new hybrid organic-inorganic membranes have been developed from poly(ether etherketone) (PEEK) sulfonated with concentrated sulfuric acid, the resulting polymer being called SPEEK. In order to improve water retention and barrier properties, zirconia has been incorporated in the polymer by *in situ* hydrolysis of zirconium alcoxide, whereas protonic conductivity was expected to be improved by incorporating HPW. The membranes were submitted to adsorption tests in water and ethanol solution and pervaporation in water and ethanol solution at 55°C. Adsorption tests show that incorporation of ZrO_2 alone did not increase significantly the level of water or ethanol solution adsorbed. However, when HPW was used this levels increased, due to high HPW hygroscopicity. Pervaporation tests showed a reduction of ethanol permeability of the membrane by incorporating ZrO_2, resulting on an increase of the barriers properties. The nanostructural features of the membranes were investigated by SAXS. SAXS curves of the pure SPEEK membranes in the dried state are characteristic of polymers presenting local density fluctuations without nanostructural organization, whereas SAXS patterns of the same polymeric membranes containing water or ethanol exhibit an interference peak at medium q-range. The presence of this peak can be attributed to the existence of SO_3H-rich spatially correlated nanodomains containing the solvent, dispersed in a polymer matrix constituted by chain segments containing a few number of SO_3H groups. Addition of 4% in weight of zirconium oxide in SPEEK membranes containing water induces the quite disappearance of the interference peak in the SAXS spectrum. This phenomenon should be attributed to the very high affinity between the zirconium alcoxide and water, inhibiting the formation of the primary SO_3H-rich nanodomains containing water. On the contrary, the poor affinity between ethanol and zirconium oxide does not affect the formation of nanodomains in organic-inorganic membranes containing ethanol. The simultaneous incorporation of zirconium oxide and HPW in SPEEK membranes containing water or ethanol induce the complete disappearance of the interference peak associated to nanodomains: in this case all solvent interacts with HPW molecules, which are extremely hydrophilic, inhibiting nanodomains formation. In this sense, this investigation performed by SAXS is of fundamental importance to understand the effect of nanoscopic structure on membranes properties, aiming the optimization of the membranes performance.

References

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