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# Morphological properties of Nafion-$TiO_2$ composites prepared by solgel and casting.

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**Abstract** – Nafion-Titania composite membranes prepared either by casting or by sol-gel route have been studied as electrolytes for Proton Exchange Membrane Fuel Cell (PEM Fuel Cell) at high temperatures (130 ºC). Small angle x-ray scattering (SAXS), scanning electron microscopy (SEM), energy dispersive analysis using x-rays (EDAX) and impedance spectroscopy (IS) were employed to investigate the composite properties. The cast-composite membrane has a heterogeneous distribution of titania particles in the film, whereas the solgel-composite has a well-dispersion of the inorganic phase. The former composite have higher proton conductivity, while the latter has lower proton conduction, owing to the high tortuosity imposed by the dispersed insulator nanoparticles.

Titania fillers have been added to Nafion polymer to overcome PEM fuel cell low performance at high temperatures [1]. Such composites have displayed lower ohmic overpotential losses compared to the analogue polymer when the temperature is raised up to 130 ºC. Parameters such as inorganic phase distribution and specific surface area were argued to influence the fuel cell performance [1]. Both parameters are strongly altered depending on the method of composite preparation. Composite membranes Nafion-$TiO_2$ are generally prepared by two methods: solgel and casting [2]. The former comprises the synthesis of titania nanoparticles inside the film after the impregnation of the Nafion polymer with the alkoxide precursor. The later is formed by a mixture of the polymer dissolved in a suitable solvent and titania particles previously synthesized. The resulting mixture is casted in a Teflon mold. The cast-composite membrane displays higher performance than sol-gel-composite at the same particle content. Nevertheless, sol-gel composite has a higher stability under fuel cell tests during long periods [2]. The understanding of composite morphology and its influence in the cell performance are considered important breakthrough in the development of higher performance materials.

Small angle x-ray scattering measurements (SAXS) were performed to evaluate the composite nanostructure. Scanning electron microscopy (SEM) and energy dispersive using x-rays (EDAX) were carried out to study the particle distribution in the cross-section of the film. Impedance spectroscopy (IS) was used to measure the proton conductivity as a function of particle content and of temperature.

SAXS spectra of composite samples evidenced an upturn in intensity at lower angles ($q < 0.2$ Å$^{-1}$) assigned to the titania particle scattering (Fig.1). Solgel-composites SAXS spectra exhibit a shoulder in the range $q = \sim 0.03$ to $\sim 0.2$ Å$^{-1}$, which suggests a system of nanoparticles dispersed inside Nafion films, whereas cast-composites curve profile displayed no maximum of scattering. SEM images revealed a two-phase contrast of the cast composite cross-section in which the brightest face corresponds, as revealed by EDAX, to inorganic character. A heterogeneous distribution of titania particles in the cast composite film is observed. Solgel-composite micrograph displayed a regular surface and the EDAX mapping showed no preferential concentration of the inorganic phase. These results are in agreement with SAXS spectra. IS measurements showed that the addition of titania particles either by solgel or by casting has resulted in a decrease in the film proton conductivity. Moreover such a decrease is more intense for the solgel composite (Fig.2). Well-dispersed insulator filler provides a more tortuous path for proton conduction.

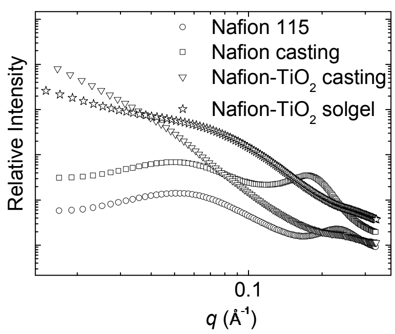


**Figure 1:** SAXS spectra of solgel and casting prepared composite membranes. Spectra of analogue polymers are shown by means of comparison.

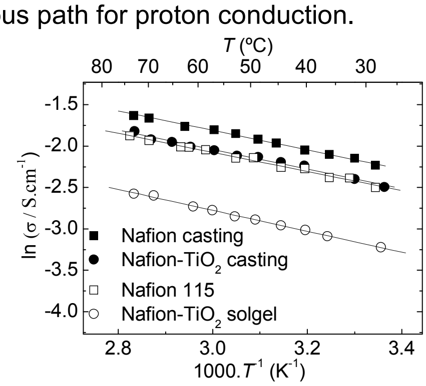


**Figure 2:** Proton conductivity dependence on temperature for composites (10wt%) prepared by solgel (open symbols) and by casting (closed symbols). Linear fits are showed.

[1] V.Baglio, et al, J. Electrochem. Soc. 152 (2005) A1373.

[2] E.I. Santiago, et al, Electroch. Acta 54 (2009) 4111.