Hybrid inorganic-organic proton conducting membranes for PEMFCs: synthesis, properties and relaxations

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Proton exchange membrane fuel cells (PEMFCs) are of intense interest to industry and the scientific community because of their high energy conversion efficiency, low environmental impact and their possibility for use in a wide variety of applications from portable electronic devices to light-duty electric vehicles [1]. At the heart of the fuel cell is a proton exchange membrane (PEM) that allows the transport of hydrogen ions, evolved at the anode, to the cathode where oxygen is reduced to water. The current prevalent PEMs feature perfluorinated main chains functionalized with perfluoroether side chains terminated with acidic -SO₃H groups. These materials (DupontTM Nafion®, Asashi Aciplex®, Dow®, 3M and Flemion®) generally are characterized by a high chemical, thermal and mechanical stability and a good proton conductivity at high hydration levels [1]. This hydration requirement limits the widespread commercial application of conventional PEMs, which have inadequate proton conductivity at temperatures above 90°C and at low values of relative humidity. Fuel cells capable of operating above 120°C at low levels of hydration would obviate the need of bulky and expensive water management modules, simplify thermal management and reduce the impact of catalyst poisons such as carbon monoxide. In an effort to overcome the limitations of conventional PEMs, this work overviews the synthesis and characterization of new PEMs alternatives to classic fluorinated polymers for application in PEMFCs. The materials are prepared according to two distinct strategies: 1) doping Nafion in order to improve its thermomechanical properties and proton conductivity or extend its operating conditions to temperatures above 100°C and anhydrous conditions; 2) synthesis and characterization of PEMs based on polybenzimidazole and polysulfone as an alternative to perfluorinated polymers.

The first strategy involves the study of two different systems obtained by doping a Nafion membrane with the [(ZrO₂)(Ta₂O₅)_{0.119}] inorganic "core-shell" nanofiller or with two different proton conducting ionic liquids, triethylammonium methanesulfonate and triethylammonium perfluorobutanesulfonate [2-4]. The second strategy focuses on the study of new PEMs polymers alternative to fluorinated such as polybenzimidazole and sulfonated poly(pphenylenesulfone) membranes, whose properties have been modulated by the addition of phosphoric acid and an hybrid filler [5] or poly(1-oxotrimethylene) and silica, respectively [6]. All of these materials are extensively characterized in terms of their thermal, mechanical, structural and electrical properties to highlight the interactions between the different components present within the membranes. These interactions govern the membranes' macroscopic properties which need to be improved in order to predict and optimize their behaviors under operating conditions in fuel cells.

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FIGURES

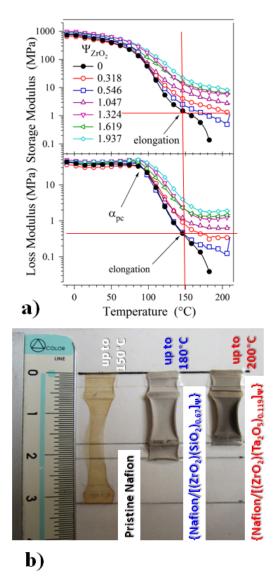


Figure 1. Effect of the doping with a "core-shell" inorganic nanofiller on the mechanical properties of hybrid inorganicorganic Nafion-based nanocomposite membranes. a) Trends of storage and loss moduli *vs*. T in {Nafion/[(ZrO₂)(Ta₂O₅)_{0.119}]_Ψ} membranes; b) samples after DMA measurements.

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