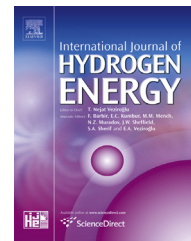


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Effect of a neutral fluorinated network on the properties of a perfluorosulfonic acid ionomer as proton exchange membrane

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ABSTRACT

Proton and water transport properties as well as water sorption, thermomechanical properties, and morphology of a new series of semi-Interpenetrating Polymer Network (semi-IPN) combining perfluorosulfonated ionomer (Aquivion[®]) with a neutral fluorinated network of composition ranging between 10 and 50 wt% have been studied. When less than 20 wt% of neutral fluorinated network are included, water and proton transport properties of semi-IPNs are enhanced compared to that of Aquivion[®], despite of their decrease of ion exchange capacity and their capacity to absorb water. Thermal and chemical stabilities are maintained very close to those of Aquivion[®]. In addition, these new materials show similar performances in fuel cell operation at 105 °C compared to those of Aquivion[®]. That evidences that perfluorosulfonated ionomer can be strengthened by association with a neutral fluorinated network.

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Introduction

At the present, the most advanced membranes in Proton Exchange Membrane Fuel Cells (PEMFCs), commercially available or incorporated into demonstrators, integrate a perfluorosulfonated acid ionomer (PFSA) as polymer electrolyte. Thus, perfluorosulfonic acid polymer named Nafion[®] is the reference membrane because of its high water and proton transport properties as well as high chemical, thermal and mechanical stabilities. However, Nafion[®], as well as other PFSA, is not suitable for operating at temperature higher than 100 °C. A main reason is the difficulty in maintaining a

homogeneous and adequate hydration rate in the membrane above this temperature when operating in fuel cell [1,2]. Dehydration results in the decrease of the proton conductivity and therefore a decrease in fuel cell performance. Another reason is the loss of its mechanical properties with increasing temperature [3–8] from its mechanical relaxation temperature followed by creep chains beyond this temperature. Finally, the gas permeability of Nafion[®] increases with temperature, so reducing also its performances.

Thus, a means of improving the properties of Nafion[®] is to combine it with another polymer having the required property. These polymer combinations can be made in various ways such as the semi-Interpenetrating Polymer Network

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(semi-IPN) architecture [9] where a linear polymer is entangled in the cross-linked host matrix. Thus, the immobilization of a polyelectrolyte through a network should avoid its high temperature creep.

To our best knowledge, only Nafion[®] has been included as linear PFSA in semi-IPN, and the main aim is to reduce the Nafion[®] methanol permeability in order to improve the Direct Methanol Fuel Cell (DMFC) performances. The various networks associated with Nafion[®] are from three types. First, hydrocarbon polyelectrolyte networks have been investigated. Among them, 2-acrylamido-2-methyl-1-propane-sulfonic acid (AMPS) network seems to be the best [10–14]. Indeed, the DMFC performances are at least equal to that of Nafion[®] when more than 60 wt% of AMPS are introduced in the Nafion[®]/AMPS semi-IPN and the methanol permeability of these semi-IPNs is similar to that of Nafion[®]. By contrast, the performances of a DMFC operating with a semi-IPN made of a poly (styrene sulfonate) network is significantly lower than those obtained with Nafion[®] [15]. Thereby, associate a polyelectrolyte network with Nafion[®] does not seem to lead to reduce its sensitivity to aging and swelling–deswelling cycles in DMFC.

Second, Nafion[®] has also been associated to a neutral hydrocarbon network such as, for example, a poly (vinylpyrrolidone) (PVP) network [16]. The advantage of this polymer type is its compatibility with Nafion[®] due to the establishment of ionic bonds between their amino groups and the sulfonic acid functions of Nafion[®], as that is also observed with networks based on poly (benzimidazole-co-N-vinylimidazole) [17]. These interactions limit the phase separation between the polymers whose characteristic size is less than 100 nm according to the SEM images. The Young modulus of these semi-IPNs is higher and simultaneously their methanol permeability is lower compared to that of Nafion[®]. According to our knowledge, only one article reports PEMFC tests with a membrane associating Nafion[®] with 3 mol% of a divinylbenzene-based network (DVB) [18]. This Nafion[®]/DVB semi-IPN has been evaluated in a fuel cell at 80 °C, 60% relative humidity (RH) and under H₂/O₂. The current density at 0.4 V is equal to 1 A/cm² which is still substantially lower than that measured with Nafion[®] (2.2 A/cm²). Finally, it is also noted that most of semi-IPNs listed until now have been synthesized by impregnating a Nafion[®] membrane into a solution of the partner network monomers which are then polymerized.

Finally, Nafion[®] has also been associated with fluorinated neutral networks. Its combination with a network based on poly (vinylidene fluoride) (PVDF) [19,20] causes the decrease of the water uptake at 80 °C from 19 to 10 wt% for Nafion[®] and Nafion[®]/PVDF (60/40) semi-IPN, respectively and to 6 wt% for the (20/80) composition. Simultaneously, proton conductivity decreases from 5 × 10⁻² S/cm for Nafion[®] to 5 × 10⁻³ and 10⁻³ S/cm for these same semi-IPNs. This is consistent with the decrease of the ion exchange capacity (IEC) of the semi-IPNs from 0.91 mmol/g for Nafion[®] to 0.19 mmol/g for Nafion[®]/PVDF (20/80) semi-IPN as the PVDF ratio increases. However, the addition of PVDF increases the Young's modulus from 10 for Nafion[®] to respectively 16.5 and 25 MPa, for the Nafion[®]/PVDF (60/40) and (20/80) semi-IPNs. Finally, these materials were tested in H₂/Air fuel cell at different

temperatures, at 100% RH. The current densities are lower than those obtained with Nafion[®]. For example, at 80 °C, the current density at 0.4 V is 0.9 A/cm² with the Nafion[®]/PVDF (80/20) semi-IPN against 1.2 A/cm² with Nafion[®]. Other polymers derived from fluorinated aromatic polyimides (FPI) [21–25] or fluorinated polybenzimidazole (PBI) [26] have also been used as the host neutral network. As previously, a decrease of water uptake and conductivity is systematically observed for semi-IPNs compared to those of Nafion[®]. However, the presence of these networks improves the mechanical properties at room temperature. On the one hand, the tensile strength of Nafion[®] (27 MPa) is almost tripled up to 80 MPa for the Nafion[®]/FPI (10/90) semi-IPN. On the other hand, its storage modulus at 50 °C ($E' = 55$ MPa) is almost 4 times higher ($E' = 220$ MPa) for Nafion[®]/FPI (80/20) semi-IPN. Thus, for all of these semi-IPNs compared to Nafion[®], water uptake, ion exchange capacity and conductivity simultaneously decrease when the amount of neutral network increases whereas the mechanical properties are systematically improved.

To summarize, include Nafion[®] in a semi-IPN architecture allows improving its mechanical properties, reducing its methanol permeability and water uptake, which should consequently lead to better dimensional stability. It turns out that fluorinated polymer-based networks, in spite of their ionic neutrality, seem to be the best partners to PFSA for PEMFC application since proton conductivity of semi-IPN remains high enough (above 10⁻³ S/cm). In addition, fluorinated polymers have better compatibility with Nafion[®] compared to hydrocarbon polymers. However, the fuel cell performances with these materials are lower than those obtained with single Nafion[®]. Among them, performances of PVDF-based semi-IPNs are the closest of those of Nafion[®]. However, PVDF contains 48 wt% fluorine while the other FPI and PBI fluoropolymers associated with Nafion contain only between 25 and 27 wt% fluorine. Thus, a key parameter to obtain better fuel cell performances is perhaps to increase the fluorine content in the partner network.

In our work, we have associated another PFSA than Nafion[®], i.e. Aquivion[®] in a semi-IPN architecture in order to increase the fluorine content in the final material. This pathway leads to a decrease of ionomer proportion and so perhaps to that of the transport properties. However, the semi-IPN architecture should modify the morphology of the hydrophobic and hydrophilic domains due to a better compatibility between these both phases. The behavior of the Aquivion should be improved for the low water amounts, i. e. at temperature above 80 °C. We made also the choice to work with Aquivion[®] as PFSA instead of Nafion[®] because Aquivion[®] has a higher relaxation temperature (127 against 67 °C) [27].

The neutral fluorinated polymer network has been synthesized from Fluorolink[®] MD 700, commercial oligomer containing the highest fluorine content (62 wt%) we found. Ion exchange capacity, and water and proton transport properties of these new semi-IPNs combining Aquivion[®] and Fluorolink[®] MD 700 were characterized. The mechanical properties and the thermal and chemical stabilities were also studied. Finally, these Aquivion[®]/FMD semi-IPNs have been tested in PEMFC at different temperatures up to 105 °C.

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