



Strengthening of perfluorosulfonic acid ionomer with sulfonated hydrocarbon polyelectrolyte for application in medium-temperature fuel cell

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ARTICLE INFO

Article history:

Received 16 November 2015

Received in revised form

2 April 2016

Accepted 10 April 2016

Available online 3 May 2016

Keywords:

Perfluorosulfonic acid ionomer

Sulfonated polyelectrolyte

Polymer blend

Mechanical relaxation

PEMFC

ABSTRACT

The mechanical properties and conductivity, as well as the water sorption and transport properties, of a new series of blends of perfluorosulfonated acid ionomer (PFSA, Aquivion[®]) and disulfonated poly(aryl ether ketone) (DS-PAEK) with compositions ranging between 10 and 90 wt% were studied. For 10–20 wt% sulfonated hydrocarbon polyelectrolyte blends, the main mechanical relaxation temperature of side chains of Aquivion[®] increased 10–20 °C as compared to pure Aquivion[®]. This shift demonstrates the presence of interactions between Aquivion[®] and DS-PAEK while the ion exchange capacity, the capacity to absorb water, and the proton conductivity of blends remained very close to those of pure Aquivion[®]. In addition, these new materials show improved robustness and better performance in fuel cell operation at 105 °C as compared to Aquivion[®]. These results indicate that PFSA materials can be strengthened by adding a sulfonated hydrocarbon ionomer.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are widely studied because of their high potential as alternative energy converters for transportation, mobile, and stationary applications. An ion-conducting polymer membrane plays the role of the electrolyte by ensuring proton migration from the anode to the cathode and water transport from the cathode to the anode. This membrane, which also acts as a gas separator, must therefore exhibit high proton conductivity, as well as high chemical, thermal, and mechanical stability. At the present, the most advanced membranes commercially available or incorporated into demonstrators integrate a perfluorosulfonated acid (PFSA) ionomer as a polymer electrolyte. Thus, the perfluorosulfonic acid polymer named Nafion[®] (marketed by DuPont DeNemours) is considered a reference membrane because of its remarkable properties. However, Nafion[®], as well as other PFSA, are expensive and they display a loss of gas and methanol barrier properties, as well as a strong drop in proton conductivity and mechanical properties with increasing temperature [1–6]. That is one of the main reasons why the current operating temperature of PEMFCs or direct methanol fuel cells (DMFCs) is limited to 80 °C. However, many applications

require higher operating temperatures, e. g. up to 120 °C, in order to improve heat removal/recovery or to enhance tolerance to pollutants, such as CO, which can be present in the fuel [7]. Consequently, numerous studies have focused on developing new membranes for PEMFCs.

Many of these current studies focus on polymer blends, which are a way to combine different properties in a polymer material [8]. However, this type of association is usually complicated because of the almost universal non-miscibility of polymers, leading to macroscopic phase separation and consequently to a heterogeneous material. In the literature, the polymers that have been successfully blended with Nafion[®] can be classified in three types: fluorinated neutral polymers, hydrocarbon neutral polymers, and polyelectrolytes. The main aim of these blends is generally to reduce the gas and methanol permeability of Nafion[®] for DMFC application.

Neutral fluorinated polymers mixed with Nafion[®] are poly(vinylidene fluoride) (PVDF) [9], a copolymer of vinylidene fluoride and hexafluoropropylene [poly(VDF-co-HFP)] [10,11] and Teflon-fluoroethylene propylene (FEP) [12]. According to the blend composition, phase separation is generally observed. If methanol permeability is effectively reduced by one to three orders of magnitude as the ratio of neutral fluorinated polymer increases, the water absorption detrimentally decreases from 37 to less than

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5 wt% and the proton conductivity decreases by ten times. However, fuel cell performance is at least similar to that of Nafion[®], and it is even improved at 60 °C with a 1 M methanol solution with a Nafion[®]/Teflon-FEP (60/40) blend as the membrane [12].

Nafion[®] has also been blended with neutral hydrocarbon polymers such as polybenzimidazole [13–15], polyvinyl alcohol [16,17], propylene oxide [18,19] or poly(1-vinyl-1,2,4-triazole) [20] and polypyrrole [21]. According to these studies, the association with neutral hydrocarbon polymers rather than with fluorinated ones allows retention of water uptake to a degree similar to that of Nafion[®] while reducing the methanol permeability and retaining the DMFC performance.

Finally, to decrease its methanol permeability, Nafion[®] is usually mixed with a polyelectrolyte. Blends of hydrogenated aromatic sulfonated polymers based on poly(ether ether ketone) (PEEK) [22,23] or poly(aryl ether ketone) [24,25] and a non-aromatic linear poly(vinylphosphonic acid) have been reported [26]. These blends generally show a micro-scale phase separation except where acid–base interactions are created between both polymers [27]. The proton conductivity of these materials is between 10^{-3} and 10^{-1} S/cm and their methanol permeability is reduced from 10^{-6} to 10^{-7} – 10^{-8} cm²/s. All these materials have a reduced water absorption ratio as compared to Nafion[®], despite the significant swelling behavior of the polyelectrolyte partner. For small amounts of sulfonated PEEK (0.5–3 wt%), the quantity of water sorbed by the blends at 25 °C is similar to that sorbed by Nafion[®] (34%) [28]. Their conductivity is reduced by a factor of 10 (10^{-3} as compared to 10^{-2} S/cm for Nafion[®]). Finally, some DMFC tests have been carried out with these membranes, and they showed better performance than Nafion[®], most probably because of a reduced methanol cross-over. For instance, at 0.3 V, the current density is 50 mA/cm² for 100 μm Nafion[®] and 75 mA/cm² for a membrane based on Nafion[®] blended with 1 wt% sulfonated PEEK.

Thus, adding of neutral polymers with Nafion[®] can lead to a decrease of the proton conductivity of the blend, in particular due to the decrease in the water uptake and in the ion exchange capacity of the materials. On the positive side, the methanol permeability is reduced. Blends of Nafion[®] with aromatic polyelectrolytes appear to be the best compromise. Indeed, proton conductivity close to that of Nafion[®] is preserved. The methanol permeability of such blends is reduced as compared to Nafion[®] while their fuel cell performance is generally better.

The goal of polymer blends involving PFSA and a polyelectrolyte based on sulfonated PEEK reported in the literature was to improve the proton conductivity of sulfonated PEEK and to reduce the methanol permeability of PFSA. In both cases, the materials were designed for DMFC and used Nafion[®] as unique a PFSA. In our work, we wanted to show that PFSA materials can be strengthened by adding a sulfonated hydrocarbon ionomer. We therefore chose to associate a linear disulfonated poly(aryl ether ketone) (DS-PAEK) with PFSA other than Nafion[®], i. e., Aquivion[®]. The ionic exchange capacity, water sorption, and proton conductivity of these new membranes were characterized. A study of the mechanical properties was also carried out. Finally, these blends were tested in a PEMFC test at different temperatures up to 105 °C.

2. Experimental

2.1. Materials

DS-PAEK in the potassium salt form [ERAS Labo, $M_n = 20\,000$ g/mol, ion exchange capacity (IEC) = 1.45 mmol/g] is a copolymer based on bisphenol 6 F, 4,4'-difluorobenzophenone, and sodium 5,5'-carbonylbis(2-fluorobenzenesulfonate). It was synthesized

according to a previously reported procedure [29]. Anhydrous N,N-dimethylacetamide (DMAc, Sigma Aldrich) was used as received. Aquivion[®] D79–20BS (Solvay Specialty Polymers, EW = 770–810 g/eq, IEC = 1.23–1.30 mmol/g) was purchased as an aqueous dispersion at 20 wt% concentration. Solid Aquivion[®] ionomer was obtained by evaporating water from the dispersion in a ventilated oven at 60 °C for 15 h. The resulting fragmented film was then crushed into a powder using a pestle.

2.2. Membrane elaboration

The membranes were elaborated as follows: Aquivion[®] and DS-PAEK were solubilized independently at 0.2 g/mL in DMAc. Adequate volumes of both solutions to obtain the desired composition were then mixed for 15 min. The mixture was then coated onto a glass plate, controlling the thickness with a coating knife, and heated at 120 °C for 24 h in a ventilated oven. The temperature of the heat treatment (120 °C) was chosen so as to be close to the glass transition temperature of Aquivion[®] ($T_g = 127$ °C [30]), making it suitable for shaping by enabling chain mobility.

Opaque and flexible Aquivion/DS-PAEK membranes were then removed from the glass plates by immersing them in water. In order to remove any traces of remaining solvent, and especially to acidify the sulfonic groups in potassium salt form, the membranes were then soaked for 24 h in 1 mol/L aqueous HCl solution at room temperature. Then, they were rinsed in deionized water several times to remove any excess of hydrochloric acid (until reaching a neutral pH).

Aquivion[®]/DS-PAEK membranes with different DS-PAEK weight proportions varying from 10 to 90 wt% were elaborated according to the same experimental protocol. They are denoted as Aquivion[®]/DS-PAEK (x/y), where x and y correspond to the weight fractions of Aquivion[®] and DS-PAEK, respectively, in the dried material. Pure DS-PAEK and Aquivion[®] membranes were also elaborated according to this protocol to be used as references.

2.3. Characterization

Prior to any characterizations, except for the fuel cell measurements, the materials were dried for 2 days at 50 °C under vacuum (5 mmHg) until they reached constant weight. This temperature was high enough to allow evaporation of the water but low enough to avoid excessive reorganization and/or side reactions in the materials.

2.3.1. Ionic exchange capacity

The ionic exchange capacity of the materials was determined by titration of protons. The dried membranes (w_0) were immersed for 3 days in 100 mL of an aqueous 2 mol/L NaCl solution at room temperature in order to exchange protons of the sulfonic groups with sodium cations. Then, 10 mL of this solution (V_{H^+}) was titrated with an aqueous 10^{-3} mol/L NaOH solution. The endpoint (V_{eq}) was determined by the color change of bromothymol occurring between pH 6.0 and 7.6. The IEC value was calculated as

$$IEC \text{ (mmol. g}^{-1}\text{)} = \frac{(C_{NaOH} \times V_{eq}) / V_{H^+}}{w_0} \times 10$$

Three measurements were systematically made with good reproducibility and their average value is reported.

2.3.2. Water uptake (WU)

Materials were subjected to water vapor at 25 °C in a sealed compartment under nitrogen flow to maintain a controlled relative humidity. Water uptake (WU) was determined from the weights of the water-swollen (W_w) and dried (W_d) materials as

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