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Proton exchange membrane based on poly-perfluorosulfonic acid modified with sulfonamide groups

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Poly-perfluorosulfonic acid membranes modified with sulfonamide groups were investigated for proton conductivity for applications in fuel cell. The degree of cross-linking by sulfonoamide groups and thermal properties, such as glass transition and degradation were investigated by means of Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). The proton conductivity as function of relative humidity (RH) at fixed operating temperature (80 ^{0}C) reaches 37 mS/cm at 80% RH. The membrane obtained after cross-linking by aqueous ammonia treatment, followed by thermal treatment has an improved thermal stability by 58 ^{0}C.

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1. Introduction

Proton exchange membrane fuel cells (PEMFC) have a wide range of applications. They are commercially available since 2002 as stack systems under different trade marks (Ballard, De Nora, ERL). Costs of such systems are strongly dependent on material performances (6,000-20,000 euro/kW [1]). In this context, research focused on three directions: 1. development of new proton conducting polymer membranes operating at high temperatures, up to 200 ºC; 2. less expensive catalysts for replacing Pt and Ru-based catalysts and 3. new advanced graphite bipolar plates [1]. Related to proton exchange membranes, the standard is perfluorosulfonated acid (PFSA) membranes due to their mechanical and chemical stability. There are some commercially available PFSA membranes, such as Nafion® (Du Pont de Nemours and Co.), Aciplex® (Asahi Chemicals), Flemion® (Asahi Glass), Dow XUS® (Dow Chemical) [3-6]. PFSA has a complex structure where three regions can be distinguished: (1) polytetrafluoroethylene backbone (PTFE), (2) $-O-CF_2-CF-O-CF_2-CF_2-$ lateral chains connecting the backbone and the third region, and (3) ionic clusters containing sulfonic acid ions. PTFE backbone ensures PFSA membrane mechanical and chemical stability both in oxidizing and reducing environments, leading to a lifetime of up to 60,000 h [2]. The super-acid behaviour is given by sulfonic acid groups (e.g. trifluoromethane sulfonic acid) which share the same carbon atom with the strong electro-negative fluorine atoms. The sulfonic groups in acidic form PFSA membrane lead to high proton conductivity, the property that makes them appropriate for fuel cell application. In dry state, dehydrated PFSA membrane acts like an isolator. In fully hydrated state, hydrogen ions within the third region reach a high mobility and travel along water molecule bonds, migrating from one sulfonic acid group site to another [6]. Conduction mechanisms are strongly dependent on pKa value, ion exchange capacity, the amount of absorbed water and percolation threshold. Zawodzinksi et al. [7] have investigated absorbed water behaviour defining percolation and phase inversion thresholds depending on the number of water molecules per sulfonic group. A major drawback of PFSA membranes is low ionic conductivity at low relative humidity (RH) and/or at high operating temperatures, because of chemical degradation processes. The proton conductivity of Nafion membrane reaches 100 $mScm^{-1}$ in full hydration state, but decreases for temperatures over water boiling point as absorbed water is lost/leaves the structure [3]. Moreover, when used in direct methanol fuel cells, cross-over effects become a limiting factor for PFSA membranes. As an attempt to tackle these issues, different methods for modifying PFSA membranes are used, such as additives (oxides: SiO_2 [8], TiO_2, ZrO_2 [9-11], silicates [12-13], heteropolyacids- phosphates [14], intrinsic semiconducting polymers [15]). Another method to improve PFSA performances is to insert $-NH_2$ groups in amine or amide form via cross-linking process. The proton mobility through the membrane and the proton concentration are strongly dependent on the cross-linking chemical process. In this context, this paper deals with physical properties of perfluorosulfonated membrane modified/ cross-linked by amine groups. The resulting membrane was investigated by thermal analysis and in plane four-electrode method.

Table 1.

Membrane type	Water content (%)	Onset temperature of thermal degradation (^{0}C) (TGA)	Ionic conductivity at 80^{0}C and 80% RH (mS/cm)
F1050	28.52	295	67.98
F1050-NH	7.85	353	36.60

2. Experimental

2.1 Materials

PFSA membrane: Fumapem 1050 (FuMA-Tech GmbH), characteristics: equivalent weight EW=1000 g/eq, specific conductivity in acidic form >85 mS/cm, water uptake 25%wt at room temperature, thickness 50-60 microns, dimensional swelling in water at 80 ^{0}C 7%, density 1.98-2 g/ccm, glass transition 110 ^{0}C, temperature of starting thermal decomposition 270-300 ^{0}C.

Other materials: Aqueous ammonia (28%), potassium hydroxide and hydrochloric acid, chemical grade for analysis, Sigma Aldrich.

2.2 Methods

Membrane conditioning*:* Fumapem F1050 in salt form was treated in 10% aqueous solution of HNO_3 for 3h at 90 ^{0}C. After rinsing with demineralised water, the membrane was boiled for 1 h at 90 ^{0}C. Then, the membranes were washed with demineralised water (~pH 7) and kept in 0.5M H_2SO_4 solution. Before immersion in monomer solution PFSA, F-1050 was dried at 80-85 ^{0}C.

The cross-linking: A Fumapem-1050 PFSA membrane in acidic form was immersed in a solution of 500 mg potassium hydroxide in 50 ml of 28% aqueous ammonia at 10 ºC for 3 hours. The membrane was then dried and heated at 200 ºC for 30 min. In the second step, the membrane was immersed in the same solution for 50 hours, followed by drying and heat treatment at 200 ºC for 30 min. This reaction ensures sulfonyl halide groups conversion into sulfonic acid salts and sulfonamide groups. The next step is a hydrolysis treatment in 10% solution of potassium hydroxide for 2 hours at 80 ºC. A 10% solution of hydrochloric acid was used for acid exchange, followed by rinsing with water and drying. The sample is further referred to as F1050-NH.

2.3 Characterization methods

Water content was calculated as follows:

$$\text{Water content } (\%)=[(M_{wet}-M_{dry})/ M_{dry}]*100$$

where M_{wet} is the weight of the membrane after soaking in water for 24 h and M_{dry} the weight of the membrane dried for 12 h at 80 ^{0}C.

FT-IR Spectroscopy was performed by FT-IR Jasco Spectrometer, model 6200 in the range 4000-400 cm^{-1}, resolution 0.25 cm^{-1}.

Thermal analyses: DSC, TGA/SDTA- Mettler Toledo, model Star1. DSC experimental conditions: heating rate 10ºC/min, temperature range is 25-350ºC, 1.5-2 mg samples are encapsulated in aluminium pans. TGA experimental conditions: heating rate 5 ºC/min, temperature range 25-400 ºC. Thermal analyses were performed in air after conditioning all membranes at RT for 24 h.

The electrical conductivity was measured via four-electrode conductivity test cell (BT-512 Membrane Conductivity Test System, Bekktech LLC, USA) at fixed temperature (80ºC). Membrane samples were cut into strips of approximately 15 mm length and 4-5 mm wide and placed in the probe cell (distance between middle electrodes, 4.2 mm) with temperature and humidity control (± 1 degree absolute accuracy) in nitrogen gas [16].

3. Results and discussion

The water content, thermal degradation temperature and ionic conductivity at 80% RH and 80^{0}C for F1050 and F1050-NH, are summarized in Table 1. The perfluorinated membrane in acidic form F1050 has shown water content of 28.52%, meanwhile for the F1050-NH a value of 7.85% was obtained. That is a consequence of cross-linking effect which reduces the hydration level. The cross-linking process improved thermal stability from 295^{0}C (F1050) to 353^{0}C (F1050-NH). In addition, the cross-linking reduced the proton conductivity from 67.98 mS/cm (F1050) to 36.60 mS/cm (F1050-NH).

FT-IR spectroscopy revealed a few structural modifications, specific cross-linking of the amine groups (Fig. 1). Both spectra show specific peaks of the perfluorosulfonated membrane backbone, similar to other reported results [17, 18], as follows: 551cm^{-1} associated to torsion vibrations t(CF_2), 626-653 cm^{-1}- rotation vibrations ω(CF_2), 717 cm^{-1}- symmetry vibrations $\nu_s(CF_2)$, 805 cm^{-1}- ν(C-S) vibration, 963-980 cm^{-1}- ν(C-O-C) vibration, 1059 cm^{-1}- symmetry vibrations $\nu_s(SO_3^-)$, 1127 cm^{-1} - asymmetry vibrations $\nu_{as}(SO_3^-)$, 1150-1243 cm^{-1}- asymmetry vibrations $\nu_{as}(CF_2)$, 1300-1319 cm^{-1}- ν(C-C) vibrations and 1471 cm^{-1}- asymmetry vibrations $\nu_{as}(SO_3H)$. In F1050-NH_3 spectrum, the 1471 cm^{-1} peak is stronger than in F1050 spectrum and there are two shoulders at 3080 cm^{-1} and 2867 cm^{-1} specific to amino groups.

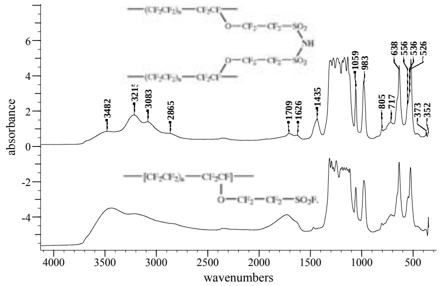

Fig. 1. FT-IR spectra of F1050 and F1050-NH membranes.

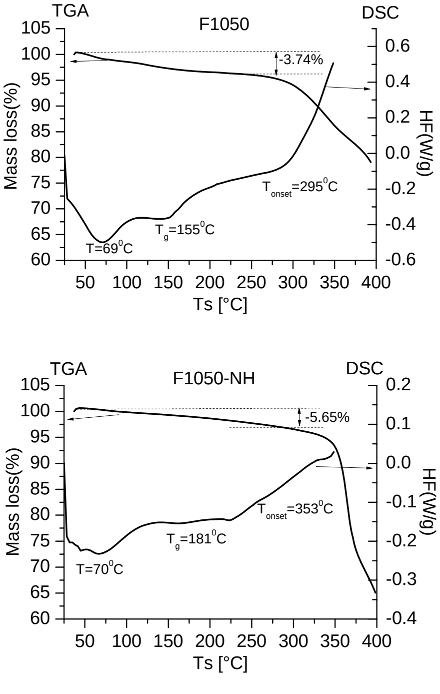

Fig. 2. Thermal behaviour of F1050 and F1050-NH – TGA and DSC (^exo).

F1050-acidic form has a typical behaviour of the perfluorosulfonated polymers (Fig. 2). The endothermic effect at 69 ºC is associated to water desorption accompanied by conformational reorientation of the molecular chains (DSC curve). For the same temperature interval, TGA curve shows a mass loss of 1.85%- the amount of released water. A glass transition appears at 155ºC due to conformational structure of PFSA backbone [19]. Another glass transition at 110 ºC is hidden by the endothermic effect of water desorption [20-22]. The onset temperature of thermal degradation is ranging in the interval 293-295 ºC in both TGA and DSC curves.

On TGA curve, there is a continuous mass loss of about - 1.9% associated to the released residual water and/or a weak dehydrogenation of pendant $-HSO_3$ groups. TGA and DSC curves of the modified F1050-NH membrane, shown in Fig. 2, reveal specific structural transformations. One can observe the same features as in F1050 membrane case with a few degree displacements. The endothermic effect associated to water desorption occurs at a temperature of 70 ºC along with other structural transformations of the macromolecular chains (DSC curve) induced by sulfonoamide group cross-linking. A mass loss of about 1% on TGA curve is associated to this transformation, corresponding to the amount of water released. The glass transition at 155 ºC in F1050 case is shifted by 26 ºC towards higher temperature. The onset temperature of thermal degradation of the cross-linked F1050-NH membrane is found within the interval 346-353 ºC in both TGA and DSC curves, that is, about 58 ºC more than for the unmodified F1050 membrane. Polymer configuration is strongly influenced by the cross-linking process occurring via aqueous ammonia reaction. The induced effects are reflected in the temperature shift of glass transition and water desorption endothermic response. Ionic conductivity measured at a fixed temperature (80 ºC) has a specific dependence on the relative humidity. In conductivity vs. relative humidity logarithmic representation (Fig. 3), there are three specific regions separated by RH =30% and RH=80%, where conduction mechanisms change. Sulfonic groups play a counter ion role in polymer branches, determining space modulated charges dependent on HSO_3 pendant group distribution and orientation. Conduction mechanisms are directly influenced by the number of water molecules, n_{H2O}, in the system and by the temperature [23-24]. F1050 membrane conductivity increases with relative humidity reaching the maximum value of ~140 mS/cm when full hydration level is achieved. The logarithm of the conductivity has a linear dependence for each of the three regions [25]. In the first region defined by the percolation threshold at RH=30%, the ionic conductivity is associated to dissociative processes with proton hopping along $-HSO_3-H_3^+O-H_2O-$ chains in PFSA microdomains. The next region, within 30 and 80% RH, shows a quasi-linear increase of the conductivity. Conduction mechanisms are governed by two competitive processes depending on dissociation rate and migration rate of hydrated protons. The slope is smaller than in the first case, as the dissociative rate is higher than the migration rate. When the rates are equal, a phase inversion occurs (RH=80%) and the polymeric matrix plasticizes.

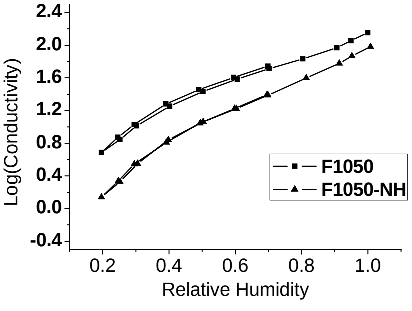

Fig. 3. Logarithmic representation of the conductivity vs. relative humidity at a temperature of 80°C for F1050 and F1050-NH membranes.

Considering PFSA as a separate nano-phase material [26], proton conduction is the result of acid site dissociation (-SO_3H pendant groups) in the presence of water confined in hydrophilic domains. Dissociated protons are transferred in the aqueous media and transported through the membrane. For lower hydration levels, conduction mechanisms are determined by proton hopping along acid sites mediated by water molecules till percolation threshold is reached [27]. Over this percolation threshold, diffusion and migration mechanisms are dominant and strongly dependent on the amount of water within hydrophilic domains. Upon sulfonoamide group cross-linking of the membrane, a change in proton conductivity is expected. As the water content of the modified membrane is smaller than for F1050 membrane, a lower value of the conductivity of the F1050-NH membrane is obtained. When the membrane undergoes the cross-linking process, hydrophilic domains rearrange affecting the proton transfer rate.

4. Conclusions

Conduction mechanisms in perfluorosulfonic acid membranes are defined by dissociation processes on sulfonic pendant groups and proton transport occurs by hopping or migration depending on membrane humidification level. Membrane cross-linking of the membrane by aqueous ammonia treatment, followed by thermal treatment, resulted in a structure with thermal stability improved with up to 58 ^{0}C, but with lower proton conductivity. Therefore, studies are to be continued for the optimization of experimental conditions and for testing alcohol permeability in order to analyse the possibility to use the membrane in direct methanol fuel cells.

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