



Proton and cesium conductivity in perfluorosulfonate ionomers at low and high relative humidity



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ARTICLE INFO

Article history:

Received 17 November 2015

Received in revised form 13 January 2017

Accepted 23 January 2017

Available online 1 February 2017

Keywords:

Membranes

Charge transport

Electrochemistry

Ionomers

ABSTRACT

Nafion exhibits one of the highest proton conductivity at room temperature and it is the standard electrolyte of proton exchange membrane fuel cells (PEMFC). However, the temperature dependence of ionic conductivity of Nafion is highly dependent on the measuring conditions and it is still a matter of debate. In the present study, detailed dielectric spectroscopy (DS) measurements in both dry (under N₂ flow) and water-saturated conditions were carried out in a broad range of temperature and frequency. Such DS results were correlated to differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) data taken in similar conditions. The main results revealed that in samples conditioned in N₂ flow (*RH* ~0%) the transport of both proton and cesium ions is coordinated with the dynamics of Nafion relaxations. In hydrated Nafion (proton form), conductivity measurements at different frequencies revealed two regimes: one at high-frequency, in which the Vogel-Tamman-Fulcher (VTF) law indicates a close relation between the polymer glass transition temperature T_g ; and, a second one at low frequency, bearing great similarity to the transport observed in nearly dry samples. The reported experimental results contribute to disentangle the intricate transport properties of Nafion.

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1. Introduction

Nafion (Dupont) is a leading polymer from a family of perfluorosulfonate ionomer membranes that are produced under different trademarks (3M, Dow, Flemion, Aciplex, Hyflon) and possesses one of the highest proton conductivity among solid proton conductors [1]. Recently, the relationship between the proton conductivity and the relaxation dynamics at a high temperature (HT) range (~80–140 °C) is pursued in order to identify the underlying mechanisms responsible for the transport properties of Nafion in HT polymer electrolyte fuel cells (PEFC). At this temperature range, polymer thermal transitions take place and can affect significantly the performance of PEFC [1,2].

In order to advance the understanding of the relation between microstructure and electric properties in Nafion at HT, the dependence of mechanical and dielectric relaxations upon water content must be taken into account [2,3,4]. It has been generally accepted that the water uptake capacity of ionomer samples is dependent on the flexibility of polymer chains, which allows polymer expansion upon water sorption. However, the water sorption of ionomers increases both the

proton dissociation and the flexibility of the polymer chains, both of which increase the proton conductivity of Nafion. Such effect makes the determination of the exact contribution to the proton conductivity of ionomers a hard task [2,3,4]. In this context, mechanical/dielectric relaxations studies dedicated to the role played by the water sorption on the flexibility and conductivity of ionomers are scarce [5,6,7,8].

Furthermore, several authors identified anisotropic water transport in Nafion at *RH* < 100% [9], suggesting that the proton conduction is preferred along one of the directions of the ionomer main chains. Therefore, the investigation of the proton conduction properties of Nafion films conditioned at *RH* ~0%, when the proton charges are mostly coordinated with the polymer chains, must be the preliminary characterization for understanding the dependence of the proton conductivity on the motion of the polymer chains. Nonetheless, the study of the conductivity of Nafion at *RH* ~0% is useful for eliminating the contribution of the water and for determining the role of the polymer relaxations to the transport properties.

A considerable data set of the proton conductivity of Nafion has been published [1–15]. However, most of the reported data was collected in a rather limited range of temperature and relative humidity. Conductivity measurements of Nafion at *RH* ~0% and the correspondence between thermal/mechanical/dielectric properties and ion conductivity at such

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condition are rarely found [5,6,8,16]. Arrhenius plots of Nafion proton conductivity at $RH \sim 0\%$ were previously reported to be composed of two distinct regimes [6,7]. At low temperatures ($T \sim 20\text{--}90\text{ }^\circ\text{C}$) Arrhenius-like temperature dependence is usually reported, whereas at higher temperatures ($T > 90\text{ }^\circ\text{C}$) a deviation from the Arrhenius behavior has been observed [6,7]. The non-Arrhenius behavior of the proton conductivity, identified as a conductivity upturn at $T > 90\text{ }^\circ\text{C}$ was fitted with the Vogel-Tamman-Fulcher (VTF) equation and related to the cooperative motion of the main ionomer chains with the charge transport [6,7,16]. Although this result is in accordance with the VTF empirical law, such measurements of the proton conductivity of Nafion at $RH \sim 0\%$ have been limited to a limited temperature range ($T \sim 20\text{--}120\text{ }^\circ\text{C}$) [7]. Dielectric spectroscopy (DS) studies have been performed at anhydrous conditions in a more extended T -range ($-155\text{ }^\circ\text{C}$ to $+155\text{ }^\circ\text{C}$) for perfluorosulfonate ionomer membranes such as 3 M membranes, Nafion and Nafion containing ionic liquids [6,8,16]. Such DS data confirmed the presence of non-Arrhenius behavior, which was considered to be a result of the VTF-temperature dependence [8,16]. The VTF behavior was also observed for Nafion β -relaxation at anhydrous condition and at low RH (the ratio $\text{H}_2\text{O}/\text{SO}_3\text{H} = 6$) [17], thereby confirming the cooperative transport between charge and segmental chain motions.

The intricate relationship between the relaxation dynamics and the proton conduction properties of nearly dry perfluorosulfonate ionomers has its counterpart in the hydrated state. Recently, it was shown that the temperature dependence of proton conduction of hydrated Nafion, measured at constant $RH = 100\%$, is similar to the one observed at $RH \sim 0\%$: an Arrhenius regime in the $T \sim 30\text{--}90\text{ }^\circ\text{C}$ range and a non-Arrhenius upturn of proton conductivity for $T > 90\text{ }^\circ\text{C}$, which could be also fit with the VTF equation [15,16]. More recent studies, performed at low water content ($\sim 3\text{--}6$ water molecules per SO_3H) and at constant water partial pressure, evidenced basically two regimes in the proton conductivity of Nafion: an Arrhenius portion of the curve up to $\sim 80\text{ }^\circ\text{C}$, followed by a decrease of proton conductivity of the ionomer at $T > 120\text{ }^\circ\text{C}$ [2]. Such results suggest that the conductivity of Nafion at constant water partial pressure is strongly dependent on the sample water content. The proton conductivity of Nafion at constant water partial pressure decreases for $T > 100\text{ }^\circ\text{C}$ due to a dramatic loss of water from the sample [2,18], whereas the proton conductivity and the water content measured in a closed system ($RH \sim 100\%$) increase in the temperature interval $40\text{--}180\text{ }^\circ\text{C}$ [11, 15]. Thus, the conductivity upturn at high T can be attributed to the increasing water uptake, while the chain dynamics plays a minor role in the charge transport.

Moreover, it is interesting to note that the temperature dependence of the proton conductivity of Nafion displays irreversibility when consecutive measurements are carried out [15]. Particularly, the non-Arrhenius portion of the conductivity curve is absent in the second heating ($RH = 100\%$). On the other hand, the polymer glass transition (T_g) is not expected to change significantly upon successive heatings [19]. Therefore, the irreversibility of the proton conductivity puts in doubt the validity of the VTF law at high T , as the VTF behavior is dependent on the polymer T_g .

Previous broadband DS studies suggested that the proton conductivity of Nafion was modulated by the motion of main and side chains [6,8]. However, the interpretation of Nafion electric/dielectric spectra is under intense debate, as different mechanisms for the same observed dielectric relaxations were given [5–8,11,20–21]. From the earliest reports on the dielectric spectroscopy of Nafion up to the present days, the dielectric relaxations were attributed to the polymer relaxations due to the correspondence with dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) [5–6,11,20–21]. Nonetheless, new interpretations of the dielectric spectra of Nafion emerged, which assigned the dielectric relaxations observed to electrode polarization phenomena [7,16]. Recently, the interpretation of the Nafion's dielectric spectra is being revisited [11,20,22] in which new findings obtained by time-dependent SAXS coupled with dc potential, and electrode

polarization characterizations suggested that the dielectric relaxations must be attributed to the polymer relaxations [22]. Nevertheless, such attributions remain controversial and different approaches are confronted [16,20,22].

In this context, the mechanism underlying the temperature dependence of proton conductivity is an open problem and no consensus has been reached concerning the role played by both the water and the relaxation dynamics on the transport properties of perfluorosulfonate ionomer membranes [8,24].

In this scenario, the investigation of the relationship between cesium conductivity-glass transition is opportune, as the glass transition temperature of Nafion in the cesium form is $\sim 130\text{ }^\circ\text{C}$, which is $\sim 150\text{ }^\circ\text{C}$ higher than the glass transition of Nafion in the protonic form [8,19].

Thus, the present study investigates the ion conductivity in a wide range of frequency, temperature, and relative humidity of Nafion, in both the proton and cesium forms, to investigate the role played by: *i*) the water content; and *ii*) the dynamics of Nafion relaxations. A good correspondence between DMA, DSC and DS adds evidences that the electric/dielectric spectra of Nafion display contributions from the bulk polymer. Moreover, the matching between the transport properties at $RH \sim 0$ and 100% shows that even at fully hydrated condition, the ion conductivity of Nafion is dependent on the mobility of the polymer chains.

2. Experimental

Commercial Nafion 115 membranes ($EW = 1100\text{ g Eq}^{-1}$) were obtained from DuPont. The membranes were pre-treated by standard cleaning and activation protocols [15]. Hydrated samples (in the protonic form) were characterized without previous thermal treatment to avoid morphological changes. To obtain samples in the cesium forms (Nafion- Cs^+), Nafion acid (Nafion- H^+) films were immersed in cesium chloride solutions (1 mol L^{-1}) at $80\text{ }^\circ\text{C}$ for 1 h. This step was repeated three times to assure a higher degree of ionic conversion. Then, samples were copiously washed with deionized water to remove the excess of reagents.

Small angle X-ray scattering (SAXS) experiments were carried out using synchrotron radiation at the SAXS beamline of the Brazilian National Synchrotron Light Laboratory (LNLS/project number 18801). Experiments were conducted with an incident wavelength $\lambda = 1.488\text{ \AA}$ in the range of the scattering vector $q \sim 0.02\text{--}0.35\text{ \AA}^{-1}$ ($q = 4\pi \sin \theta/\lambda$, being 2θ the scattering angle). Scattering patterns were collected with MarCCD detector and the intensity curves were corrected for parasitic scattering, integral intensity, and sample absorption. For in situ heated SAXS measurements as a function of temperature, N115 samples were positioned in a special sample-holder, consisting of a metallic clamps coupled with a resistive heating. The sample-holder has a $\sim 3\text{ mm}$ window for the X-ray beam and the measurements were performed in the $40\text{--}160\text{ }^\circ\text{C}$ T -range under N_2 flow.

Thermogravimetric (TGA) measurements (Setaram-LabSys) were carried out in the $25\text{--}250\text{ }^\circ\text{C}$ temperature range at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ under nitrogen flow. This setting was used to measure the mass loss of previously vacuum dried samples at $25\text{ }^\circ\text{C}$ for 1 h.

Dielectric spectroscopy (DS) measurements were performed on samples using a specially designed airtight sample holder. Such a device allows electrical measurements (through-plane) controlling both the temperature (from room temperature up to $T \sim 200\text{ }^\circ\text{C}$) and the relative humidity (RH , from ~ 3 to 100%) [1]. Temperature controllers connected to band heaters placed externally around the cylindrical sealed chambers are monitored by thermocouples (type K) inserted inside its metallic walls. Nafion samples were sandwiched with carbon cloths between stainless steel spring-load contact terminals, insulated from the chamber walls. The carbon cloth electrodes are treated in nitric acid solution and excess deionized water to remove impurities ensuring that these electrodes can be considered blocking electrodes. Before studying the electric properties of the ionomer samples, several experiments were

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