



Thermal annealing on free volumes, crystallinity and proton conductivity of Nafion membranes

Chongshan Yin^a, Zheng Wang^a, Yi Luo^a, Jingjing Li^a, Yawei Zhou^a, Xiaowei Zhang^a,
Haining Zhang^b, Pengfei Fang^a, Chunqing He^{a,*}

^a Key Laboratory of Nuclear Solid State Physics Hubei Province, School of Physics and Technology, Wuhan University, Wuhan, 430072, China

^b State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, China

ARTICLE INFO

Keywords:

Nafion
Free volume
Thermal annealing
Crystallinity
Proton pathway

ABSTRACT

Free volumes, backbone mobility, crystallinity and proton conductivity of Nafion membranes upon thermal annealing were intensively studied. The development of size and distribution of free volumes in Nafion membranes as a function of environmental humidity was found to be closely associated with the adsorbed water molecules and the Nafion backbone mobility. Results suggested a gradual decrement in Nafion backbone mobility as a function of annealing temperature, due to the thermal induced recrystallization. This was further supported by a linear decrement in the o-Ps intensity as a function of membrane crystallinity, because o-Ps atoms mostly annihilated in the amorphous phase in Nafion. Particularly, a significant increment in crystallinity was found in Nafion membranes annealed at temperatures higher than 140 °C. The present results showed that annealing at ~140 °C of Nafion membranes is favourable for their proton conductivity because of the low crystallinity.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are known as one of the most promising alternative power sources, because of their excellent properties such as inherent electrochemical functionality, good chemical stability, high power density, fast start-up, and low environmental contamination. In the industrial PEMFCs, proton exchange membrane (PEM) is one of the key components which provides proton conduction between fuel and oxidant [1–4]. Among many ion-conductive polymers, perfluorinated sulfonic-acid (PFSA) ionomers based membranes (e.g. Nafion) are widely used in fuel cell applications due to its remarkable physical and chemical stabilities at moderate temperatures [4–7]. Nafion is a random copolymer, in which perfluoroether side chains terminated with sulfonic acid groups ($-\text{SO}_3\text{H}$) are randomly distributed along the semicrystalline polymer skeleton (perfluoroethylene) [6]. The hydrophilic-hydrophobic nature of the sulfonic acid groups and the polymer backbones results in natural phase separation in hydrated Nafion membranes. Thus, three phases can be found in hydrated Nafion: semicrystalline Nafion backbone, ionic-water clusters, and an amorphous region between the Nafion backbone and ionic-water clusters [1–3]. This phase separation is responsible for unique proton transport capabilities of Nafion. Generally, proton transportation in Nafion is often considered as the proton hopping

aided by water molecules and the 'vehicular' transport of protons forming a hydrated ion (H_3O^+) [8,9].

Solution recasted Nafion membranes are commonly prepared by using Nafion precursor and followed by a thermal annealing treatment [10]. During thermal annealing, two thermal transitions (endothermic peaks) have been observed at 95 ~ 150 °C and 230 ~ 260 °C, respectively [11–14]. These thermal transitions are commonly suggested to be associated with microstructure variations in Nafion, such as changes in crystallinity and electrostatic network. However, explanations regarding these thermal transitions are quite different. It's known that many properties such as proton conductivity, gas separation and mechanical behavior of Nafion membranes are strongly impacted by their thermal history [15–17]. Therefore, a deeper understanding of the annealing effects on the ionomers is required, and it is very meaningful to study the dependencies of hole free volume, crystallinity, proton conductivity and mechanical property on the thermal annealing of Nafion membranes [7,18,19].

It's known that the atom-sized free volume holes are abundant in polymers and are extremely important for various properties of polymers [20–22]. Positron annihilation lifetime spectroscopy (PALS) is a widely used, nondestructive tool for measuring vacancy-type defects [23–25], pores [26–28], open-volumes [29–33] in various materials. Recently, PALS technique has been extensively applied to study the

* Corresponding author.

E-mail address: hecq@whu.edu.cn (C. He).

microstructural variations in polymers induced by dynamic humidity, temperature and material doping [7,21,34–36]. After being injected in a polymer, some of incident positrons combine with electrons from adjacent atoms to form the positronium (Ps) atoms. There are two spin states Ps, namely spin-antiparallel para-positronium (p-Ps) and spin-parallel ortho-positronium (o-Ps). The lifetime of o-Ps (τ_{o-Ps}) is of great importance for the characterization of hole free volumes in polymer [7,36]. In a vacuum, o-Ps undergoes the 3γ annihilation and its intrinsic lifetime is as long as 142 ns? Whereas, being localized in hole free volumes in polymers, o-Ps undergoes 2γ pickup annihilation and the τ_{o-Ps} drops to a few nanoseconds. The exact value of τ_{o-Ps} in polymers depends on the free volume hole size and is influenced by the overlapping of the o-Ps wave function with the electron layer on the wall of free volume. The formation probability of o-Ps (the intensity of o-Ps, I_{o-Ps}) is determined by the density of free volume holes in the polymer as well as the chemistry of polymers [37,38].

In this study, the impacts of thermal annealing on free volumes in Nafion membranes as a function of relative humidity were investigated. Water uptake, swelling ratio, crystallinity, mechanical property and proton conductivity were further studied for Nafion membranes annealed at different temperatures. The results provide a deeper understanding of the mechanics of thermal history governing the microstructure and proton conductivity in Nafion membranes.

2. Material and methods

2.1. Membranes preparation

Commercial Nafion solution (DuPont, DE-520, EW 1100, 5 wt% of perfluorosulfonate resin (H^+ form) and 50 wt%/45 wt% of isopropanol/water mixture) was used in this study, and all Nafion membranes were prepared by a self-assembly sol-gel process. Firstly, 5 wt% Nafion solutions were placed in a flat-bottomed quartz dish at 25 °C for 12 h. Then, the resulted Nafion membranes were annealed at different temperatures (from 120 °C to 200 °C) in a vacuum for 4 h. Membranes are denoted by the corresponding annealing temperatures as Nafion-120, Nafion-140, Nafion-160, Nafion-180 and Nafion-200. Prior to measurements, the membranes were cleaned through a standard procedure [7]. Thickness of the prepared membranes was $65 \pm 5 \mu m$ and no visual evidence of macro-phase segregation was found. Deionized water (purified with Milipore, resistivity = $18 M\Omega cm^{-1}$) was used in this work, and all the other solvents and chemicals were of reagent grade and were used as received.

2.2. Swelling behavior, density, thermal analysis and X-ray diffraction (XRD) measurements of the membranes

The geometrical expansion (swelling ratio) of Nafion membranes was calculated from the variation in volumes of dry (V_{dry}) and water saturated (V_{wet}) Nafion membranes [39]. Thickness of membranes was measured by a micrometer screw gauge with a resolution of 1.0 μm , and was reported as an average of three measurement points for each strip-shaped membrane. Length and width of membranes were measured with a vernier caliper of 0.02 mm resolution. The membrane density (ρ) was derived from membrane weight M_0 (M_{wet} or M_{dry}) along with the length (L), width (W) and thickness (T) of membrane using the following equation,

$$\text{membrane density } \rho \text{ (g cm}^{-3}\text{)} = \frac{M_0}{(L \times W \times T)} \quad (1)$$

The indices *wet* and *dry* denote the values of wet (immersed in water) and dry (kept in the nitrogen atmosphere for several days) Nafion membranes, respectively. The M_{wet} was measured for Nafion membranes after wiping out the surface adsorbed water using tissue paper. Measurements of swelling behavior and density of Nafion membrane were conducted three times for each membrane at 25 °C, and

the mean values were presented as the final results. Differential scanning calorimetry (DSC) thermograms of un-annealed Nafion membranes were collected on a Perkin-Elmer DSC-7 at 5 °C min⁻¹ under nitrogen purge. Prior to the measurements, membranes were first dried under vacuum at 60 °C for 5 h. The XRD measurements were performed for dry Nafion membranes on a D8 ADVANCE type diffractometer at room temperature, and the scan rate was 4° min⁻¹.

2.3. Water uptake, ion exchange capacity (IEC), mechanical property, positron annihilation lifetime and proton conductivity measurements

Positron annihilation lifetime spectroscopies and proton conductivity, mechanical property, water uptake and ion exchange capacity (IEC) of Nafion membranes were measured. Details of experiments and characterizations can be found in the Supplementary Materials and our published work [7].

3. Results and discussion

3.1. Thermal annealing on water uptake and swelling behavior of Nafion membranes

Table 1 shows the water uptake, IEC and density of Nafion membranes annealed at different temperatures. Obviously, increasing annealing temperature from 120 °C to 200 °C results in no apparent change in IEC, however, water uptake of Nafion membranes decreases moderately. Simultaneously, with increasing annealing temperature, no significant variation is found in the density of dry Nafion membranes (ρ_{dry}), while the wet membrane density (ρ_{wet}) increases dramatically. Because of the swelling behavior, ρ_{wet} are basically lower than ρ_{dry} . Thus, the increment in ρ_{wet} indicates a degradation of swelling capacity of Nafion membranes. Fig. S1 shows the effects of annealing temperature on the swelling behavior of Nafion membranes. Clearly, the swelling ratio of Nafion membranes drops from 148% to 124% with increasing annealing temperature from 120 °C to 200 °C. The poor swelling ratios of Nafion membranes annealed at higher temperatures are attributed to a decrement in the mobility of Nafion backbones upon thermal treatment, because for PFSA's such as Nafion, there is a dynamic ionic-cluster transition associated with the long-range mobility of molecular chains around the temperatures of 95–150 °C [9,13,40]. Being thermally annealed above this transition temperature, Nafion molecular chains retain sufficient mobility to rearrange and pack themselves to form crystallites. The crystallites acting as physical cross-links always reduce the mobility of Nafion molecular chains [6], thereby suppress the swelling and water uptake of overall Nafion membranes. The actual transition temperature of the present Nafion membranes will be discussed later in this study.

Generally, in hydrated Nafion membranes, the water channels for proton transportation can be formed due to the interconnection of ionic-water clusters, which is greatly beneficial to proton transportation among the membranes [7,41]. As a key factor of proton transportation ability of Nafion membranes, the water content of Nafion membranes as a function of ambient humidity has been investigated and results are shown in Fig. S2. Clearly, Nafion-120 and Nafion-140 membranes exhibit the highest water contents at various humidities. From point of

Table 1
IEC, water uptake and density of Nafion membranes.

Annealing Temperature	IEC (mmol g ⁻¹)	Water Uptake (%)	Density (Dry/Wet) (g cm ⁻³)
120°C	0.90 ± 0.02	26.5 ± 0.7	2.11/1.80
140°C	0.92 ± 0.02	26.3 ± 0.7	2.08/1.82
160°C	0.89 ± 0.02	23.6 ± 0.7	2.11/1.98
180°C	0.91 ± 0.02	21.7 ± 0.6	2.10/2.03
200°C	0.89 ± 0.02	20.3 ± 0.5	2.13/2.07

Download English Version:

<https://daneshyari.com/en/article/7919961>

Download Persian Version:

<https://daneshyari.com/article/7919961>

[Daneshyari.com](https://daneshyari.com)