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# Effect of Water on the Size Distribution of Free-Volume Holes in Nafion Membrane

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**Abstract.** Positron lifetime spectroscopy was employed for investigation of the size distribution of free volume holes in Nafion N-1110 membrane. Size distribution of free volume holes was determined in the as-received and dried membrane and in the membrane immersed in water at various temperatures. It was found that absorbed water causes reduction of the mean size of free volume holes and increase of their dispersion and concentration. This indicates that free volumes are split by swollen ionic clusters absorbing water. The kinetics of water uptake and the amount of absorbed solvent were determined by *in-situ* measurement of the weight increase.

## Introduction

Nafion is perfluorosulfonated cation exchange membrane developed by du Pont de Nemours & Co. Inc. Nafion exhibits relatively complicated mesoscopic structure consisting of hydrophobic polytetrafluoroethlylene (PTFE) skeleton and hydrophilic ionic clusters [1]. High proton conductivity together with excellent thermal and chemical stability make Nafion very attractive for applications in gas separation processes and fuel cells. Nanoscopic free volume holes facilitate gas transport through membrane providing suitable pathways. Therefore, characterization of the size distribution of free volume holes in Nafion is very important. Ortho-positronium (o-Ps) is a unique probe of nanoscopic free volume holes due to pick-off annihilation process which makes the o-Ps lifetime dependent on the size of free volume hole where o-Ps is confined [2,3]. In this work we employed positron lifetime (LT) spectroscopy for investigation of the influence of water solvent on the size distribution of free volumes holes in Nafion membrane.

## Experimental

We studied Nafion membrane N-1110 ($H^+$ form, equivalent weight = 1100 g/eq) provided by du Pont de Nemours & Co. Inc. Specimens for LT measurements were multi-stacks consisting of four membranes each with thickness of 0.254 mm tightly attached to each other to ensure that all positrons are stopped inside the sample. LT measurements we performed on a digital spectrometer with excellent time resolution of 145 ps (FWHM $^{22}$Na) [4]. A $^{22}Na_2CO_3$ positron source with activity of 1 MBq deposited on 2 μm thick mylar foil was always sandwiched between two identical specimens. LT spectra were decomposed using a least square fitting program LT (version 9) [5]. The model function consists of (i) a contribution of positrons annihilated as particles represented by discrete exponential components; (ii) positronium (Ps) contribution described by a complex component consisting of a short-lived discrete para-positronium (p-Ps) component with lifetime $\tau_{p\text{-}Ps}$ and a long-lived o-Ps component represented by a continuous log-normal distribution of annihilation rates [5]; (iii) the source contribution consisting of two weak components with lifetimes of approximately 368 ps and 1.5 ns and corresponding intensities of approximately 8% and 1% representing a contribution of positrons annihilated inside the source spot and in the mylar foil, respectively. The effect of water on the size distribution of free volume holes was studied in Nafion immersed in redistilled water (resistivity 18.7 MΩ at 25°C).

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## Results and Discussion

**As-received and dried Nafion.** Table 1 shows results of LT investigations of as-received Nafion membrane. The contribution of positrons annihilated as particles consists of two components: the shorter component with lifetime $\tau_1 \approx 200$ ps can be attributed to free positrons while the longer component with lifetime $\tau_2 \approx 430$ ps comes from positrons trapped at free volumes. The Ps component consists of a short-lived p-Ps component with lifetime $\tau_{p\text{-}Ps} \approx 130$ ps and a long lived o-Ps component characterized by the mean lifetime $\tau_{p\text{-}Ps} \approx 3.1$ ns and dispersion $\sigma_{o\text{-}Ps} \approx 1.0$ ns.

**Table 1** *Results of LT measurements of as-received and dried Nafion membrane. The uncertainties of fitted parameters (one standard deviations) expressed in units of the last significant digit are given in the parenthesis.*

| **positrons** | $\tau_1$ **(ps)** | $I_1$ **(%)** | $\tau_2$ **(ps)** | $I_2$ **(%)** | |
|---|---|---|---|---|---|
| as-received | 205(9) | 5.2(8) | 430(3) | 80(1) | |
| dried 130°C/2h | 204(8) | 6.0(5) | 442(5) | 80.1(4) | |
| **Ps** | $\tau_{p\text{-}Ps}$ **(ps)** | $I_{p\text{-}Ps}$ **(%)** | $\tau_{o\text{-}Ps}$ **(ns)** | $I_{o\text{-}Ps}$ **(%)** | $\sigma_{o\text{-}Ps}$ **(ns)** |
| as-reveived | 130(5) | 3.7(4) | 3.10(3) | 11.1(4) | 1.06(6) |
| dried 130°C/2h | 130(6) | 3.5(4) | 3.09(2) | 10.5(4) | 1.00(3) |

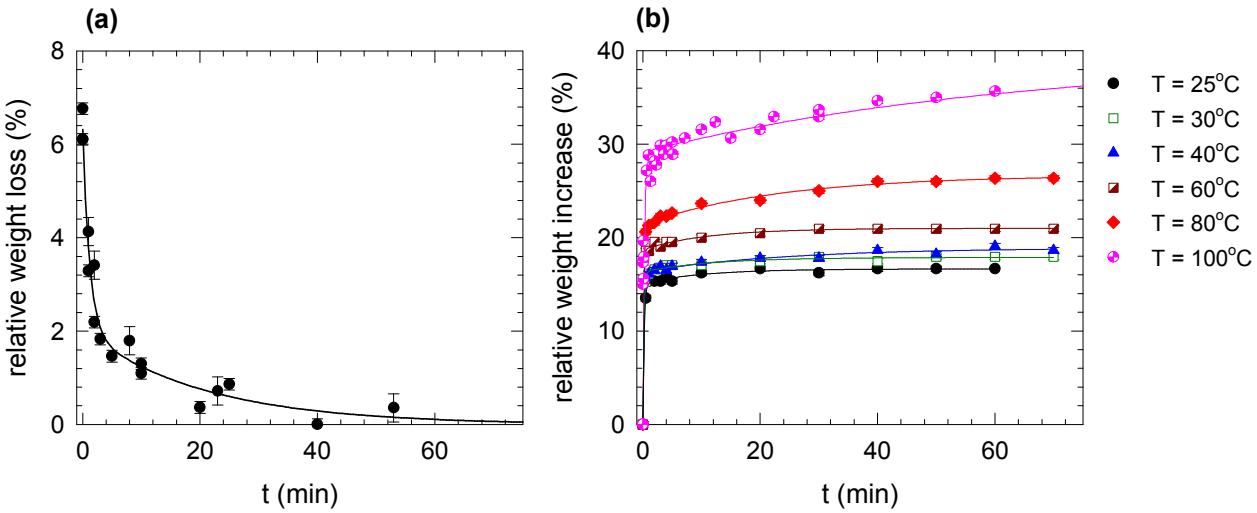


**Fig. 1** *(a) Relative weight reduction of as-received Nafion membrane dried at 130°C, (b) Relative weight increase of Nafion immersed in water at various temperatures.*

To determine water content in as-received Nafion the membrane was dried at 130°C. Fig. 1(a) shows relative weight loss of the membrane during drying. It was found that as-received membrane contains 6.7 ± 0.8 wt.% of water at ambient conditions. LT measurement of Nafion sample dried at 130°C for 2h revealed that drying did not cause any significant changes of positron parameters.

**Nafion with water.** Fig. 1(b) shows the relative weight increase of dried Nafion immersed in water at various temperatures. Obviously the amount of absorbed water strongly increases with temperature. There are two modes of water absorption into Nafion; (i) fast process occurring in time scale shorter than 1 min and representing a dominating mode of water absorption responsible for more than 80% of total water uptake and (ii) slow process which leads to further increase of water content in Nafion in the time scale of several tens of minutes. Two swelling processes in Nafion were disclosed also by SAXS and SANS investigations [6].

The effect of absorbed water on LT results is shown in Fig. 2. Water absorbed in hydrophilic ionic clusters causes a significant volume expansion of Nafion which is reflected by an increase of positron lifetimes $\tau_1$ and $\tau_2$, see Fig. 2(a). The influence of absorbed water on free volumes can be seen in behavior of the o-Ps component. The mean lifetime of the o-Ps component $\tau_{o\text{-}Ps}$ plotted in Fig. 2(c) decreases with increasing water content indicating that the average size of free volume holes was reduced. The dispersion of the o-Ps component $\sigma_{o\text{-}Ps}$ firstly increases, i.e. the size

distribution of free volume holes becomes broader, and than it decreases again. The Intensity of the Ps component $I_{Ps}$ increases with water content indicating increasing concentration of free volume holes. The size distributions *H(R)* of free volume holes were obtained from distribution of o-Ps lifetimes using the Tao-Eldrup model [2,3] and assuming spherical holes with various diameter *R*. Fig. 3(a) shows the size distributions *H(R)* scaled to the Ps yield, i.e. multiplied by the intensity $I_{Ps}$ of the Ps contribution in LT spectrum. Clearly, the size distributions of free volume holes in as-received and dried Nafion are very similar. The sample boiled in water for 30 s (water content 34 wt.%) exhibits significantly broader size distribution of free volume holes with maximum shifted to smaller sizes. In sample boiled for 2 h (water content 46 wt.%) the maximum of the distribution is shifted slightly back and the distribution becomes very narrow.

Water absorbed in hydrophilic ionic clusters causes two important morphological changes in Nafion: (i) overall volume expansion which increases the mean size of free volume holes and (ii) penetration of swollen ionic clusters into free volumes and bonding between water and sulfonic acid which may lead to splitting free volume holes into parts. In the sample boiled in water for 30 s only the fast mode of water absorption took place, i.e. the sample volume expanded due to absorbed water and at the same time some free volumes were split into parts while other remain continuous. This is reflected by a broad size distribution *H(R)*, see Fig. 3(a). In the sample boiled in water for 2 h additional water was absorbed by the slow process leading to ordering or re-arrangement of hydrophobic PTFE polymer chains [6] and formation of bonds between water and sulfonic acid. In this sample almost all free volumes are split and their size becomes relatively uniform which is reflected by a narrow size distribution *H(R)*, see Fig. 3(a). Obviously splitting of free volumes results in increased density of free volumes holes reflected by increased Ps yield, see Figs. 2(d).

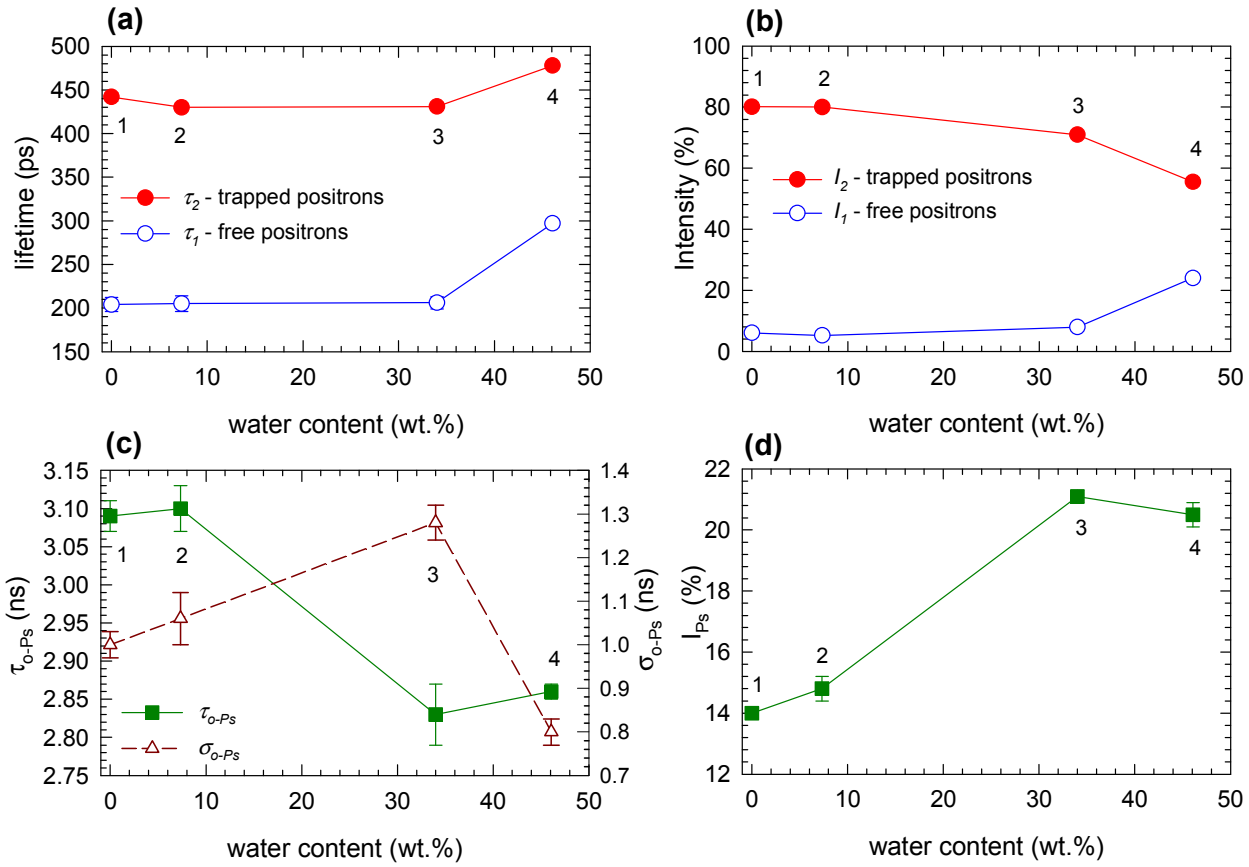


**Fig. 2** *Results of LT measurements of Nafion membrane with various water content: (a) lifetimes $\tau_1$, $\tau_2$ and (b) relative intensities $I_1$, $I_2$ of positrons annihilated as particles; (c) the mean lifetime $\tau_{o\text{-}Ps}$ and dispersion $\sigma_{o\text{-}Ps}$ of the o-Ps component; (d) intensity of the Ps contribution $I_{Ps} = I_{o\text{-}Ps} + I_{p\text{-}Ps}$. 1- dried sample (130°C/2 h), 2- as-received sample, 3-sample boiled in water for 30 s, 4-sample boiled in water for 2 h.*

The mean free volume $V_{mean}$ obtained from the size distribution of free volume holes is plotted in Fig. 3(b) as a function of the water content. One can see in the figure that $V_{mean}$ firstly decreases (and the distribution becomes broad) and then it slightly increases again (and the distribution becomes narrow). The mean free volume $V_{mean}$ determined in Nafion N-117 by Sodaye et al. [7] is plotted in Fig. 3(b) as well. It is clear that $V_{mean}$ determined in Ref. [7] agrees well with our results.

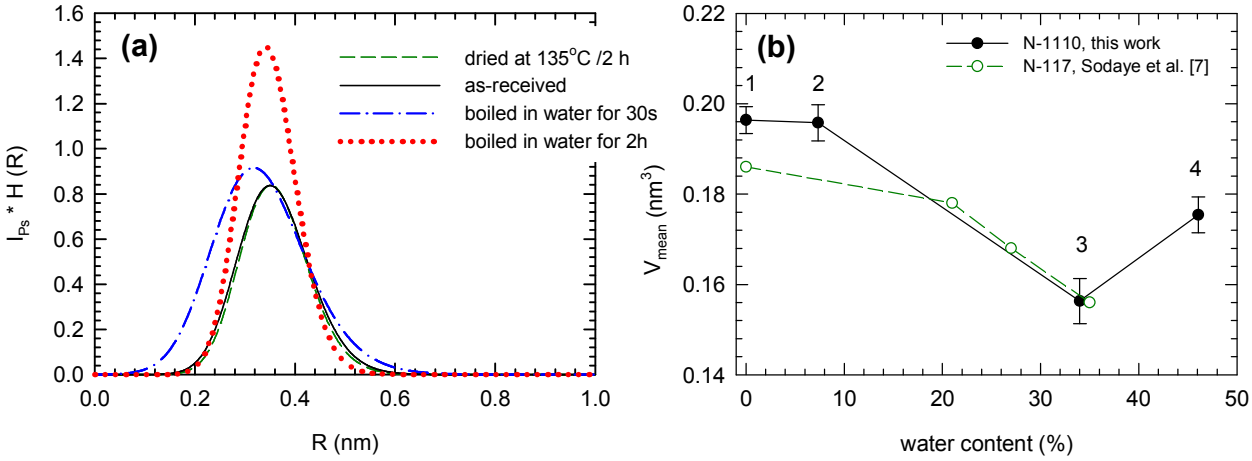


**Fig. 3** *(a) Size distribution of free volume holes H(R) scaled to Ps yield, i.e. multiplied by intensity of the Ps component* $I_{Ps} = I_{p\text{-}Ps} + I_{o\text{-}Ps}$*, (b) the mean free volume* $V_{mean}$ *plotted as a function of the water content in Nafion. 1- dried sample (130°C/2 h), 2- as-received sample, 3-sample boiled in water for 30 s, 4-sample boiled in water for 2 h. Open circles show* $V_{mean}$ *determined in Ref. [7].*

**Summary**

Influence of water on the size distribution of free volume holes in Nafion membrane N-1110 was studied in this work. It was found that as-received membrane contains 6.7 wt.% of water at ambient conditions. The water uptake is realized by two processes with different rates and the net amount of absorbed water increases with temperature. Water is absorbed in hydrophilic ionic clusters and causes a significant volume expansion of the membrane. At the same time absorbed water leads to a reduction of the mean size and an increase in the concentration of free volume holes. This is due to swollen ionic clusters which expand into free volumes and reduce the free volume size. Moreover, the expansion of ionic clusters into free volumes accompanied by formation of bonds between water and sulfonic acid which causes splitting of free volume holes into parts.

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