



Evidence for depth-dependent structural changes in freeze/thaw-cycled dry Nafion[®] using positron annihilation lifetime spectroscopy (PALS)

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ABSTRACT

The effects of freeze/thaw (F/T) cycling on the structure of dry Nafion[®] membranes were investigated using positron annihilation lifetime spectroscopy (PALS). The method correlates the lifetime and relative intensity of positrons (anti-electrons) annihilating in the open-volume voids of the membrane with void size and void volume fraction. The results, though still preliminary, show freeze/thaw-induced collapse in the pore volume near the surface of the dry membrane, and also some evidence of slight differences in the two sides of a given membrane. The work demonstrates the utility of the method in studying depth-dependent changes in membrane total free volume along with pore size, structure, configuration and environment as the result of thermal and structural stresses.

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1. Introduction

Nafion[®] (perfluorosulfonic acid) polymer electrolyte membrane (PEM) was the first successful solid-polymer electrolyte with sufficient durability and transport properties for fuel cell and electrolyzer developers to use to replace liquid-acid electrolytes, which required wicking electrode separators. (Nafion[®] is a registered trademark of E.I. DuPont de Nemours & Co.) The PEM permits easier assembly and permits electrochemical designs where gas-pressure differentials across the electrolyte are required. Interest in PEMs, like Nafion[®], from the automotive industry has been intense for the development of PEM fuel cells for electric vehicles. During the lifetime of automotive fuel cells, many cycles of freezing and warming are expected in North American and European applications. The effects of such extensive freeze/thaw (F/T) cycling of dry Nafion[®] have been examined as a baseline for freeze/thaw studies of humidified membranes. F/T cycling has been limited to -40°C to $+80^{\circ}\text{C}$ well below the glass transition, T_g , temperature of the material. In general, the most pronounced effects were a decrease in water absorption, a decrease in ultimate tensile strength, and a decrease in oxygen permeability [1,2]. There is also evidence of an increase in contact resistance between the membrane and catalyst layer against the flow field [3]. In this paper, we will present evidence for depth-dependent physical changes in the membrane's nano-scale

free-volume voids that may be intrinsically responsible for these observed macroscopic effects.

Positron annihilation lifetime spectroscopy (PALS) provides a means of comparing changes in free-volume pore size and structure, which accompany physical changes and stresses in the material. PALS is sensitive to all free-volume pores (both isolated and interconnected) in the size range from 0.3 to ~ 30 nm and to the closed-to-open pore transitions, in hydrophilic regions [4,5]. The method has been employed to measure free-volume pore size and its relation to oxygen permeability in polymer membranes [6]. In this technique, positrons are embedded in the material, where they combine with an electron, forming positronium (P_s —the bound state of the electron and its anti-particle, the positron), which diffuses into, and traps in, the free-volume voids where it exists for a short period of time before annihilation into gamma rays. In this manner, the P_s lifetime can be measured and then correlated with the electronic structure and pore size of the polymer free space using the well established Tau-Eldrup model [7]. In the Tau-Eldrup model the positronium lifetime in the void, τ_3 (in ns), is related to the pore radius by

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + \Delta R} \right) \right]^{-1}$$

where R is radius of a pore cavity surrounded by an electron cloud of thickness ΔR which is empirically determined to be 0.16–0.17 nm. The free-space pore volumes of nine diverse polymer membranes, including Nafion[®], show an excellent correlation with the diffusion constant for oxygen [6]. In addition, the measured intensity

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Table 1
Summary of the bulk-PALS fitting results.

Sample	P_s lifetime (ns)	Average pore diameter (nm)	P_s intensity (%)
Baseline	2.98 ± 0.01	0.717 ± 0.0015	9.7 ± 0.1
F/T cycled	2.91 ± 0.01	0.708 ± 0.0015	8.2 ± 0.1

The P_s lifetime is converted to a pore diameter using a spherical pore model.

of the lifetime components nominally relates to the concentration of free-volume sites in the polymer matrix. It is important to note that there is no significant bond breaking, which can occur in Nafion[®] from the limited flux of gamma rays as shown in experiments conducted in the development of de-tritiation electrolysis systems where the membrane was dosed with up to 530 kilograys (kgy) without change in properties [8].

2. Experimental

Sheets of untreated Nafion[®] N112 (1100 equivalent weight, 50 μm thickness) membranes as received from DuPont, Inc., were cycled between -40°C and $+80^\circ\text{C}$ in low humidity 365 times using 80-min cycle times to examine changes in the membrane, which might be induced over the operating range of a PEM fuel cell vehicle. The samples were sealed at a typical ambient humidity, $\sim 20\%$ relative humidity (RH), prior to cycling. Coupons of N112 membranes also maintained at $\sim 20\%$ RH were later used as baseline material for comparison.

Baseline (i.e., untreated, uncycled) and cycled coupons were cut and sealed in Ziploc[®] bags (S.C. Johnson & Son, Inc.) for bulk-PALS analysis along with (but not in contact with) a small porous package of lithium bromide salt hydrate ($\text{LiBr}\cdot\text{H}_2\text{O}$). The package was formed of microporous Tetratex[®] polytetrafluoroethylene (Donaldson Co.) sealed with Kapton[®] polyimide adhesive tape (DuPont, Inc.). The membrane was allowed to equilibrate to a constant controlled humidity of 6% RH prior to analysis, resulting in a residue of 1–2% water in Nafion[®] (DuPont, Inc.) by weight. After removal of the desiccant package, PALS was conducted on the samples within the Kapton envelopes, so the membranes could be kept dry throughout the measurements.

Initially, bulk-PALS was used to probe the average pore volume throughout the bulk of the Nafion membranes. The bulk-PALS technique uses a sodium-22 radioactive source on the sample to implant positrons throughout the entire membrane depth. For this series of membranes, we were required to stack 16 sheets of N112 to insure complete stopping of positrons. To prevent the diffusion of the radioactive source into the Nafion, sodium-22 is deposited on and encapsulated between thin (12 μm) Kapton[®] sheets that stop less than 6% of the incident source positrons. (Kapton does not form positronium and hence does not affect the measured Nafion P_s lifetime.) The deduced pore diameters are found to be close to those measured in Nafion[®], which was first humidified, then dried at 90°C so minor amounts of residual water content should not be important [9].

Table 2
Beam-PALS results at 5 keV for the Nafion[®] samples.

Membrane	P_s lifetime (ns)	Spherical pore D (nm)	Average pore D (nm)	Side-to-side D ratio	P_s intensity (%)
Baseline					
Side 1	3.32 ± 0.02	0.761 ± 0.0025	0.728 ± 0.002	1.095 ± 0.007	7.8 ± 0.1
Side 2	2.82 ± 0.03	0.695 ± 0.0035			5.4 ± 0.1
F/T cycled					
Side 1	3.08 ± 0.05	0.731 ± 0.006	0.718 ± 0.005	1.038 ± 0.013	2.5 ± 0.1
Side 2	2.88 ± 0.06	0.71 ± 0.007			2.1 ± 0.1

The P_s lifetime and the P_s relative intensity of annihilation in the pores are fitted from the spectra and the pore diameter, D is deduced using a spherical pore model. Note the low intensity of P_s annihilating in near-surface voids of the F/T-cycled sample (shaded cells).

Beam-based PALS was used to compliment the bulk-PALS measurements and characterize the surfaces of the membranes. A comparison of these two spectroscopies can reveal bulk vs. surface effects produced by the F/T cycling. Briefly, in beam-PALS positrons from a commercial 50 mCi sealed sodium-22 source are moderated using annealed nickel foils in ultra high vacuum and are then electrostatically focused on the sample into a 2 mm diameter spot at energies ranging from 0.5 keV to 5 keV. For this series of beam PALS measurements, we used a beam of 5 keV positrons to probe only the top 0.5- μm layer near each membrane surface. Only the highest available positron beam energy was used for the membranes to avoid distortions to the spectrum due to backscattered high energy P_s . While beam PALS requires the sample be placed in a vacuum, the membrane was maintained at room temperature. Thus, the amount of residual water should be close to that present in the bulk PALS measurement since further desiccation would require both vacuum and a temperature of 140°C over 24 h [10]. Such a treatment would bring the membrane above the glass transition temperature, T_g , and create additional physical changes. Details of the two experimental setups, methods, and theory can be found in the literature [4].

During the course of this work, it was noted that the pore structure was different on the two sides of the as-received membranes analyzed with Beam PALS. These were arbitrarily referred to as Side 1 and Side 2. Because of the manner in which samples were prepared, it was not possible to relate the two sides back to the original role of material purchased from Dupont[®].

3. Results

The results of the average bulk PALS and the beam PALS near-surface spectroscopy are presented in Tables 1 and 2 respectively. Freeze/thaw cycling has two bulk effects compared to the uncycled membrane: the average P_s lifetime in the F/T-cycled pores is reduced by a small (but statistically significant) amount corresponding to an overall $4.0 (\pm 0.8)\%$ reduction in average pore volume, and there is a concomitant decrease in the relative intensity of P_s annihilating in these pores from $9.7 \pm 0.1\%$ to $8.2 \pm 0.1\%$. Although the relative P_s intensity is not as straightforward to interpret as the P_s lifetime-to-pore volume correlation, a sizable decrease in the intensity *together with* a modest reduction in P_s lifetime due simply to F/T cycling strongly suggests the cycled membrane has, on average, fewer and slightly smaller free-volume pores. The beam-PALS results indicate that the distribution of free volume pores is not uniform across the membrane's thickness.

The beam-PALS results at 5 keV implantation energy are surprisingly much more pronounced, as seen in Table 2. Each membrane was examined on both sides (the sides are arbitrarily labeled "side 1" and "side 2"). There is a side-to-side difference in P_s lifetime in fresh samples that is significantly reduced after F/T cycling. However, the average lifetime measured by beam-PALS of P_s annihilating in the 0.5- μm surface layers of the membrane is nominally the same as that measured in the bulk of the membrane indicating that the pore size is uniform throughout the membrane. The interesting

Table 3
Major changes in dry Nafion 112 physical properties as a result of F/T cycling [2].

Property	Baseline	F/T cycled
MD tensile strength at break (MPa) ^a	14	10
XD tensile strength at break (MPa) ^a	10	7
MD tensile elongation (%) at break ^a	1293	39
XD tensile elongation (%) at break ^a	324	25
20 °C O ₂ permeability (cm ³ mil/ft ² h atm)	197	85
40 °C O ₂ permeability (cm ³ mil/ft ² h atm)	240	117

^a Measured while equilibrated with deionized water at 80 °C.

effect, however, is the enormous difference in the relative P_s intensity of the F/T-cycled membrane surface where P_s annihilation from the pores is all but eliminated. We note that there is also a significant decrease in relative P_s intensity in the surface region of the uncycled membrane relative to its bulk result, but *the virtual extinction of P_s annihilation from the F/T cycled membrane surface region implies this surface region is nominally devoid of any free volume capable of trapping P_s !*

Average free-space pore diameters reported for 175- μm -thick Nafion[®] N117 membranes with bulk-PALS were slightly less (0.708 nm) [11] than those for N112 measured by us, possibly because of different treatment histories and/or different measurement protocols.

4. Discussion

Pore size, including free-volume and water-filled volume, has been studied in Nafion[®] using a variety of techniques including neutron and X-ray diffraction and gas diffusion. The diameter of pores created by clusters of sulfonate groups depends on the level of hydration, which drives swelling. Water-containing pore diameters of 2–20 nm are observed in the hydrophilic regions dominated by sulfonate groups [12–14]. The solvent-free regions and those defined by the backbone polymer below the glass transition, T_g (~ 108 °C), are generally accepted as free-volume and are substantially smaller than the solvent-occupied regions. This supports the model of Nafion[®] involving hydrophilic, solvent-filled pores connected by more narrow hydrophilic channels and dominated by the hydrophobic main chain of the polymer. Previous PALS measurements on wet Nafion[®] humidified to different levels showed that the total free space volume increases, but with decreasing pore diameters, as the hydrophilic, ionic regions were swelled with water [11]. The work examined the distribution of pore sizes at different water contents, showing that the probability density functions for the water-swelled material were narrower, but with a larger area under the peak.

The clear implication in the present study is that F/T cycling of dry Nafion induces strong depth-dependent inhomogeneity in the pore volume. The virtual extinction of P_s in the F/T membrane at 5 keV is presumably uniform in the top 0.5 μm of the material. We cannot determine the complete pore volume depth profile because our beam cannot implant positrons beyond the mean depth of about 0.5 μm . However, since the average bulk P_s intensity in the F/T-cycled membrane is $\sim 20\%$ lower than that of the uncycled (baseline) membrane (see Table 1), it is reasonable to suspect a $\sim 20\%$ reduction in overall void volume in the membrane. Also, since the near-surface region has effectively no void volume, then for example, one possible void profile would have the top 5 μm at each surface lacking voids (almost completely densified) with the remaining underlying 40 μm being unaffected. This simple three-layer model might help account for the 50% decrease in oxygen permeability observed in the F/T cycled dry Nafion and the decrease in ultimate tensile strength (Table 3). These earlier studies also showed no significant loss in the percent of water take-up

in fully swollen membrane and no loss in ionic conductivity in the hydrated membrane. The implication is that the loss in free-volume caused by structural relaxation and rearrangement is primarily in hydrophobic backbone regions not containing water and the densification caused at the surface by F/T cycling is reversible on re-humidification.

Using a wide range of positron beam energies of 3–18 keV, Algiers and co-workers were able to determine depth profiles of glassy polymers [15]. Thus, a more detailed investigation of free-volume depth profiling in Nafion should be possible, although this was not the purpose of the present work. The particular beam we used can only go up to 6 keV and we selected 5 keV as our most reliable beam energy that is also high enough to be free of the systematic errors discussed in Section 2 so that we could interpret decreases in the positronium intensity as definitively due to a near surface effect on the free-volume. The slight differences in our assumed positron implantation profile and mean depth ($m = 2$ Makhovian) compared to the more rigorous work reported in Algiers is not particularly relevant to our final conclusions, but we include it as a reference because it is one of the only such works on glassy polymers.

The slight differences between the two surfaces of the membrane in both baseline and F/T membranes are believed to be the result of the manufacturing process and may be the result of different rates at which the two sides cool after the precursor material (sulfonyl fluoride form) is extruded. Since the extrusion process used to form the precursor and its subsequent base hydrolysis to make the sulfonic acid form may be intrinsically asymmetric, the resulting pore size distribution on the two sides is expected to be different. The beam PALS technique determines only the average pore diameters near the membrane surface, so that changes in structure in the hydrophilic and hydrophobic regions cannot separately be determined. While the influence of F/T cycling on an individual side of a membrane cannot be commented on in this work, it is clear that the two sides of a membrane become more similar in pore structure.

The application of percolation theory to measurements of ionic conductivity across the membrane has shown that at or above 10% membrane hydration, there are continuous hydrophilic channels throughout the material connecting regions of clustered sulfonate groups [16]. In the dry membrane surface, probed with beam-PALS, there is no indication of pore interconnection, and hence there is a range of closed pore shapes and sizes, which the PALS measurement averages.

5. Conclusions

Positron annihilation lifetime spectroscopy (PALS) provides important depth-dependent information about pore size and free space volume in ionomers, like Nafion[®], which may provide a fundamental structural understanding for physical changes which occur due to thermal cycling. The beam-PALS technique permits the examination of a thin surface layer while the bulk-PALS method permits examination of open space volume (both interconnected and closed) averaged over the full thickness of the membrane material. Extensive freeze/thaw cycling of dry N112 produces a relatively insignificant average pore size reduction, but the void volume fraction as revealed in the relative intensity of P_s annihilating in voids near the membrane surface is severely reduced. This suggests pore collapse preferential to the surface rather than a global reduction in void fraction or pore size. The interior of the membrane appears to be nominally unaffected. The effect of PEM fuel cell performance which a dry membrane is F/T cycled is expected to be minimal with the possible exception of time required for re-humidification after multiple shut-downs in cold climates.

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References

- [1] R.C. McDonald, C. Mittelsteadt, E. Thompson, Freeze-thaw cycling of proton exchange membranes: electrochemical and mechanical analysis, in: 2nd European PEFC Forum, Lucerne, Switzerland, June 30–July 4, 2003.
- [2] R.C. McDonald, C. Mittelsteadt, E. Thompson, Effects of deep temperature cycling on Nafion[®] 112 membranes and membrane electrode assemblies, *Fuel Cells* 4 (2004) 1.
- [3] E.-A. Cho, J.-J. Ko, H.Y. Ha, S.-A. Hong, K.-Y. Lee, T.-W. Lim, I.-H. Oh, Characteristics of the PEMFC repetitively brought to temperatures below 0 °C, *Journal of the Electrochemical Society* 150 (2003) A1667.
- [4] D.W. Gidley, H.-G. Peng, R.S. Vallery, Positron annihilation as a method to characterize porous material, *Annual Reviews in Material Research* 36 (2006) 349.
- [5] J.N. Sun, Y.F. Hu, W.E. Frieze, D.W. Gidley, Characterizing porosity in nanoporous thin films using positronium annihilation lifetime spectroscopy, *Radiation Physics and Chemistry* 68 (2003) 245.
- [6] V.P. Shantarovich, Positron annihilation study of polymer membrane materials, *Journal of Nuclear and Radiochemical Sciences* 2 (2001) R23.
- [7] S.J. Tao, Positronium annihilation in molecular substances, *Journal of Chemical Physics* 56 (1972) 5499.
- [8] Y. Iwai, T. Yamanihi, K. Isobe, M. Nishi, T. Yagi, M. Tamada, Distinctive radiation durability of an ion exchange membrane in the SPE water electrolyzer for the ITER water detritiation system, in: *Proceedings of the 7th International Symposium on Fusion Nuclear Technology, ISNT-7 Part A*, vol. 81, 2006, p. 815.
- [9] H.S. Sodaye, P.K. Pujari, A. Goswami, S.B. Manohar, Probing the microstructure of Nafion[®]-117 using positron annihilation spectroscopy, *Journal of Polymer Science Part B-Polymer Physics* 35 (1997) 771.
- [10] B. MacMillan, A.R. Sharp, R.L. Armstrong, An N.M.R. investigation of the dynamical characteristics of water absorbed in Nafion[®], *Polymer* 40 (1999) 2471.
- [11] H.S. Sodaye, P.K. Pujari, A. Goswami, S.B. Manohar, Measurement of free-volume hole size distribution in Nafion[®]-117 using positron annihilation spectroscopy, *Journal of Polymer Science Part B-Polymer Physics* 36 (1998) 983.
- [12] K.S. Sportsman, J.D. Way, C.C. Wen-Janq, G.P. Pez, D.V. Laciak, The dehydration of nitric acid using pervaporation and a Nafion[®] perfluorosulfonate/perfluorocarboxylate bilayer membrane, *Journal of Membrane Science* 203 (2002) 155.
- [13] M.W. Verbrugge, R.F. Hill, Transport phenomena in perfluorosulfonic acid membranes during the passage of current, *Journal of Electrochemical Society* 137 (4) (1990) 1131.
- [14] G. Xie, T. Okada, water transport behavior in Nafion[®] 117 membranes, *Journal of Electrochemical Society* 142 (9) (1995) 3057.
- [15] J. Algers, P. Sperr, W. Egger, G. Kogel, F.H.J. Maurer, Median implantation depth and implantation profile of 3–18 keV positrons in amorphous polymers, *Physical Review B: Condensed Matter and Materials Physics* 67 (12) (2003) 125404.
- [16] W.Y.H. Hsu, J.R. Barkley, P. Meakin, Ion percolation and insulator-to-conductor transitions in Nafion[®] perfluorosulfonic acid membranes, *Macromolecules* U13 (1980) 198.