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# NAFION® MEMBRANES STUDIED BY POSITRON ANNIHILATION SPECTROSCOPY

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Several Nafion® membranes have been irradiated with gamma-rays with doses ranging between 86 kGy and 960 kGy and the degradation of their properties was investigated by Positron Annihilation Spectroscopy (PAS). The post-irradiation characterization was simultaneously performed using Coincidence Doppler Broadening Spectroscopy (CDBS) and Positrons Annihilation Lifetime Spectroscopy (PALS). The studies revealed that the mechanisms for gamma-irradiation degradation of Nafion® show remarkable properties and evidenced two stages in the evolution of the hydrophilic and hydrophobic regions present in the polymer structure.

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## 1. Introduction

The durability of the polymeric materials, such as Nafion® (DuPont) under extreme operating conditions is an important consideration when using a Proton Exchange Membranes Electrolyzer for the separation of hydrogen isotopes. One of the main concerns for the adoption of Nafion® (DuPont) for Polymer Electrolyte Membrane Electrolyzer systems to be used in tritium isotope separation is the degradation of the polymer membrane because of the beta radiation produced by the tritium decay. Tritium decay gives off beta radiation that has relatively low average decay energy of about 5.69 keV.

Testing polymer membranes with tritiated water is difficult because of the safety concerns and due to the amount of time needed for membrane exposure. Therefore, gamma irradiation is often used as a substitute for beta irradiation for durability testing and comparisons are made at equivalent radiation doses.

The concept of free volume is critical for explaining and understanding the physical behavior of polymers. In polymers the local free volume holes or cavities of atomic and molecular dimensions arise due to the irregular packing of the chains in the amorphous state (static) and molecular relaxation of the polymer chains and terminal ends (dynamic and transient state). The presence of these holes means that the density of the polymer samples are about 10% less than the densities of the corresponding crystalline state.

Nafion® is a perfluorinated polymer that contains small proportions of sulfonic ionic functional groups [1]. As a result of the electrostatic interactions, these ionic groups tend to aggregate to form tightly packed regions referred to as clusters [2]. The presence of these

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electrostatic interactions between the ions and the ion pairs enhance the intermolecular forces and thereby exert a significant effect on the properties of the parent polymer.

The hydrophilic regions of the polymer are the free voids occupied with the aggregated ionic groups, while the hydrophobic regions can be identified as the unoccupied free voids [3, 4].

A positron injected into a polymer can annihilate with an electron either directly or via a bound state $e^+$–$e^-$ called positronium (Ps). The intrinsic lifetime of Ps in its singlet state, i.e. *para*-Ps (*p*-Ps), is only 0.125 ns, whereas the intrinsic lifetime of its triplet state, i.e. *ortho*-Ps (*o*-Ps), is 142 ns. The observed lifetime of *o*-Ps in substances is reduced to a few nanoseconds due to the so called pick-off process, i.e. the annihilation of $e^+$ from the interior of Ps by an electron in the environment of Ps.

The statistical ratio of the formation probability of *p*-Ps to *o*-Ps is 1:3.

Positrons and positronium (Ps) are highly sensitive to open volumes in a material; their sensitivity ranges from monovacancies (positrons) to voids or pores of 10 nm in cross-section (positronium).

The experimental and methodical combination of CDBS and PALS offers coherent information on both the size of free voids or pores in polymers and also on the chemical neighborhood of the annihilation.

Namely, measuring the coincidence Doppler broadening of the 511 keV radiation produced by various molecules can be related to the annihilation at specific sites within molecules.

PALS spectrum of a polymer is usually resolved into three exponential components related to annihilations of *p*-Ps, "free" positron and *o*-Ps. The lifetime parameter of the third component can be easily found by fitting procedures.

This paper describes a study targeting the determination of the main way for polymer degradation under the direct attack of gamma rays. The induced decomposition was tracked by Positron Annihilation Spectroscopy (PAS): Coincidence Doppler Broadening Spectroscopy (CDBS) and Positron Annihilation Lifetime Spectroscopy (PALS).

## 2. Experimental

The 100 μm thick Nafion® membranes that were investigated in this study were acquired from Ion Power Inc. [5].

The gamma irradiation of the Nafion® membranes was performed with a $^{60}$Co source with an activity of about 488 Ci; various gamma doses were obtained at different distances from the $^{60}$Co source - for details on the irradiation procedures see Table 1. The samples were exposed to the gamma-ray field during one-week. Table 1 also summarizes the absorbed gamma doses.

PAS measurements were conducted with a complex experimental set-up that allows to perform simultaneously two kinds of measurements, i.e. CDBS and PALS which are carried out with two separate data acquisition systems.

The experimental set-up for CDBS measurements [6-8] consists in two HPGe detectors operating in a back-to-back geometry that measure the energy of the two annihilation gamma-rays. The resolution of the HPGe detectors is about 1.2 keV at 511 keV, permitting the study of the Doppler broadening.

A sandwich made out of the polymer samples and the positron source is placed between these two semiconductor detectors. The positron source is a droplet of $^{22}$Na wrapped in a 5 μm thickness Mylar envelope; the activity of the positron source was 1 μCi. Each of the two identical Nafion® samples was put on an aluminum holder, the positron source being pressed in-between them.

The data acquisition system is based on a CAEN VME ADC, an USB communication bridge and a PC. The software was custom designed in order to acquire, store and examine the CDBS data [6-8].

PALS experimental set-up is based on a commercially available ORTEC system [9], with a warranted time resolution of 200 ps measured with a narrow energy window using a $^{60}$Co source. Because of the very low activity of the positron source used in these experiments, a broader energy window was chosen and consequently the time resolution was about 320 ps for 6.37 ps per channel.

*Table 1 - Irradiation condition for Nafion® membranes under investigation.*

| Sample | Distance from the $^{60}$Co source (cm) | Dose (kGy) |
|---|---|---|
| Nafion® | - | 0 |
| Nafion® 10 | 10 | 86 |
| Nafion® 7 | 7 | 176 |
| Nafion® 5 | 5 | 345 |
| Nafion® 4 | 4 | 540 |
| Nafion® 3 | 3 | 960 |

## 3. Data Analysis

The extraction of CDBS data is based on the use of shape factor in order to describe the behavior of the free volumes [10].

Since the background in the region of the wings is drastically reduced in CDBS method, then an accurate study of the wing factor by means of a relative comparison between the axial momentum densities becomes possible.

In our case, the thickness of the polymeric membranes is large enough to thermalize and annihilate all emitted positrons. Since the spectrum of $^{22}$Na source covers a broad energy domain and the emerging positrons have large thermalization ranges, one can conclude that our CDBS measurements are volume-oriented.

For each investigated polymer sample, the function $\rho$, equal to the longitudinal momentum density versus the longitudinal momentum was calculated.

One of the samples - characterized by the corresponding $\rho_{\text{reference}}$ function - was taken as a reference, and a new function called $\Delta$ was defined as:

$$\Delta = \frac{\rho - \rho_{reference}}{\rho_{reference}}$$

The software we developed permits the extraction of $\Delta$ function from every pair of samples; the energy calibration of both detectors was necessary for the calculation of the longitudinal momentum.

The PALS data were analyzed with LT v.10 program [11-12]. LT software uses along with the data for the samples also the contribution of the positron source (lifetimes and relative intensity), the resolution curves parameters, the background and zero time channel. These parameters for the source and resolution were assumed independent of measurement time and therefore they were constrained to be the same for all spectra in the series.

## 4. Results and discussions

As it was already mentioned, two kinds of positron spectroscopy measurements have been performed on Nafion® gamma-irradiated samples: CDBS and PALS.

For the CDBS measurements a non-irradiated Nafion® polymer served as reference. One must emphasize that the regular chemical structure of the Nafion® polymer is responsible for the momentum distribution of the electrons that can annihilate with the positrons, therefore the main contribution to the positron annihilation is due to this regular chemical structure of polymer.

Fig. 1 presents the evolution of the Δ function for Nafion® membranes irradiated from 86 kGy to 960 kGy.

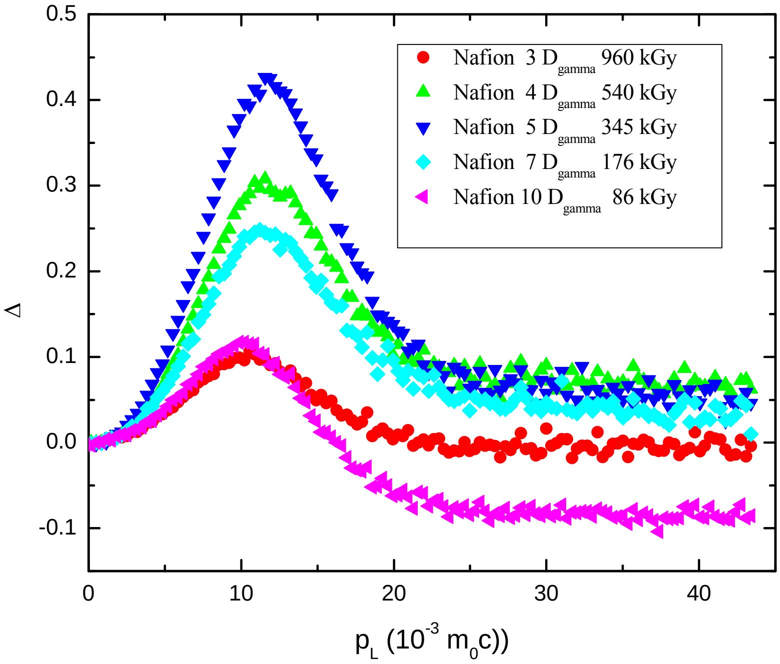

*Fig. 1. Momentum density relative to the non-irradiated Nafion® membrane*

The results of the PALS fits are presented in Fig. 2.

All spectra for Nafion® polymer samples were analyzed together, keeping as common free parameters the relative intensities of the components, the lifetime for *p*-Ps and free positrons and leaving as local free parameters the lifetime of the *o*-Ps. The mean value of the fit variance was 1.2.

The best common free parameters obtained were:

*o*-Ps Intensity = 28%, *p*-Ps Intensity = 10%, Intensity for free positrons = 62%, Mean lifetime for free positrons = 460 ps and Mean lifetime for *p*-Ps = 140 ps.

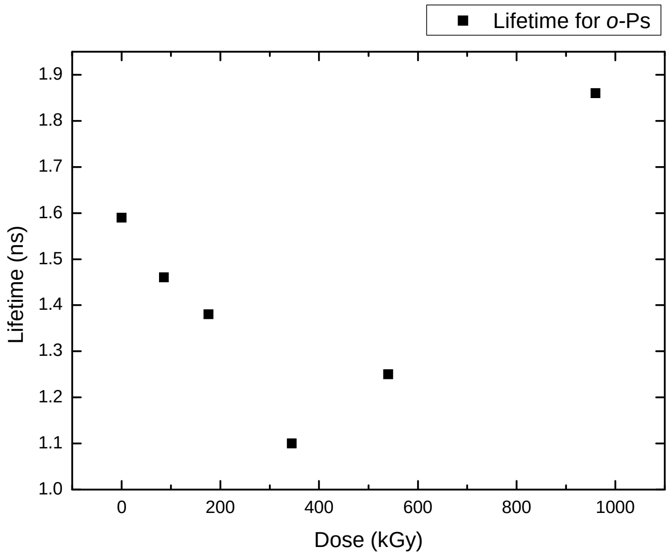

*Fig. 2. o-Ps Lifetime for Nafion® membranes.*

Increasing the gamma irradiation dose from some tens of kGy, the longitudinal momentum increases up 345 kGy and then starts to decrease; the behavior of the Nafion® 10 irradiated at 86 kGy is quite similar with the one of Nafion® 3 irradiated at 960 kGy. Somehow similar, the lifetime of *o*-Ps decreases down to 1.1 ns for Nafion® 5 sample irradiated with 346 kGy and then increases very quickly for larger gamma doses.

One can easily observe that using both PAS methods, the vicinity of the dose at which sample Nafion® 5 was irradiated - namely around 345 kGy - represents a turning point in the behavior of the polymer irradiated samples. Namely, CDBS spectrum of Nafion® 5 sample exhibits the largest longitudinal momentum for the electron-positron annihilation pair, while PALS data conducted to the shortest lifetime for the *o*-Ps, namely 1.1 ns.

Our interpretation for this peculiar behavior is related to the sulfonic ionic functional groups. As already discussed in the **Introduction**, the free voids in Nafion® are either hydrophilic (filled with sulfonic functional groups tightly packed) or hydrophobic (empty voids). It seems that the gamma irradiation deposits much of the energy in these hydrophilic regions destroying step-by-step the quasi-crystalline structure. By destroying the structure, the chemical structure of the free volumes walls is changing; fast electrons from broken chemical bonds are available for pick-off and that is reflected in the increase of the longitudinal momentum of the annihilation pair from CDBS spectra. At the same time, *o*-Ps has a shorter lifetime because of the increase in the electron density from the walls, leading to an increase of the pick-off probability.

By further increasing the gamma irradiation dose, an important decrease in S-O stretching for the sulfonic groups is taking place and so the hydrophilic regions cease to exist and new covalent chemical bonds are formed in the walls of the former hydrophilic free volumes.

As it can be seen in CDBS spectra shown in figure 1, for samples Nafion® 4 and Nafion® 3~~,~~ the longitudinal momentum of the annihilating pair decreases, reaching for the sample irradiated at 960 kGy sample the same value as for the one irradiated at 86 kGy. This is an indication of a decrease in the broken chemical bonds having fast electrons available for annihilation. The lifetime of *o*-Ps starts to rapidly increase due to the large free volumes formed from the former hydrophobic and hydrophilic regions that merged together.

Similar results were found by means of other methods, such as InfraRed Spectroscopy, fluoride emission, etc. [13] and along with the studies reported in this paper one can conclude that if irradiated with large gamma-ray doses, Nafion® membranes degrade losing their remarkable properties that allow them to serve not only a stable platform or template, but also as a catalyst. Moreover, gamma irradiation seems to affect the durability of the polymeric materials under extreme operating conditions, and their important use for Proton Exchange Membranes Electrolyzer in the separation of hydrogen isotopes is thus compromised.

## 5. Conclusions

A set of complex PAS measurements - both CDBS and PALS - has been performed on Nafion® membranes irradiated with gamma-rays doses from 86 kGy to 960 kGy. Both positron annihilation methods assessed the degradation of the remarkable properties of Nafion® membranes correlated to the values of gamma irradiation doses. A turning point in the distribution of longitudinal momentum of the annihilating pairs and in the lifetime of *o*-Ps was observed for Nafion® polymer membranes irradiated at 345 kGy.

The results obtained through the application of the two PAS methods are in agreement with other previously published scientific papers on polymer degradation under gamma-ray irradiation, such studies being relevant for the potential use of the Nafion® membranes as Polymer Electrolyte Membrane Electrolyzer systems for tritium isotope separation.

## Acknowledgements

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## References

[1] Nafion® is a registered trademark of E.I. DuPont de Nemours & Co.
[2] G. B. Butler, K. F. O’Driscoll, G. L.Wilkes, J.M.S.-Rev. Macromol. Chem. Phys. **C34**(3) 325-373 (1994).
[3] H. J.Yeager, A. Eisenberg, in: Perfluorinated Ionomer Membranes; eds. A. Eisenberg and H. L. Yeager, ACS Symp. Ser. No.180, (American Chemical Society: Washington, DC, 1982) 1-6, 41-63.
[4] P. J. Brookman, J. W. Nicholson, in: Developments in Ionic Polymers, vol. 2; eds. A. D. Wilson and H. J. Prosser, (Elsevier Applied Science Publishers: London, 1986) 269-283.
[5] http://www.ion-power.com/ NAFION® is a registered Trademark of E.I. du Pont de Nemours Company and is used under license by Ion Power, Inc.
[6] A. Vasilescu, L. Craciun, A. Ghita, O. Constantinescu, F. Constantin, C. Chiojdeanu, N. Zoita, A. Kiss, D. Bojin, P.M. Racolta, Appl. Surf. Sci. **255**(1), 46 (2008).
[7] F. Constantin, L. Craciun, O. Constantinescu, I. Ghita, C. Ionescu, P. M. Racolta, M. Straticiuc, A. Vasilescu, V. Braic, C. Zoita, A. Kiss, D. Bojin, AIP Conf. Proc. **1099**, 960 (2009).
[8] F. Constantin, C. Barna, E. Barna, M. Straticiuc, I. Burducea, Digest J. Nanomat. Biostr. **6**(2), 543 (2011).
[9] Positron Lifetime Picosecond Timing System - http://www.ortec-online.com/download/Positron-Lifetime-Picosecond-Timing-System-PLS-SYSTEM.pdf.
[10] Jean, Y. C., Mallon, P. E., Schrader, D. M. (eds.), Principles and Applications of Positron and Positronium Chemistry, World Scientific Publishing, New Jersey, London, Singapore, Hong Kong (2003).
[11] Kansky, J., Nucl. Meth. Instr. A **374**, 235 (1996).
[12] Kansya, J., Suzuki, T., Rad. Phys. Chem. **76**, 759 (2007).
[13] Fox, E. B., Greenway, S. D., Clark, E. A. Radiation Stability of Nafion® Membranes used for Isotope Separation by Proton Exchange Membrane Electrolysis, Materials Science & Technology, Savannah River National Laboratory Aiken, SC 29808 SRNL-STI-2009-00296.