Investigation of Polyethylene Electrolyte Membrane in Different Thickness with Positron Annihilation Lifetime Spectroscopy

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Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is a promising future energy source of high power density and zero-emission; for portable, stationary, and transportation devices [1]. The electrolyte membrane selectively allows positive ions and protons to pass from anode to cathode and prohibits electrons, forcing external load current. For hydrogen fuel cells, the cell membrane's proton conductivity plays a crucial role in the system's overall performance. The fluorinated polymers, such as Nafion® membranes, are the most commonly used membranes due to their high proton conductivity and stability [2]. As the free volume of the material governs the proton conduction, investigating the free volume size and density is a matter of great interest [3]. In this study, the free volume size of three different commercial Nafion® membranes were calculated by measuring the ortho-positronium lifetime from Korea Atomic Energy Research Institute (KAERI) positron annihilation lifetime spectroscopy (PALS) system.

Material & Method

❖ Positron Annihilation Lifetime Spectroscopy System

- The KAERI PALS system consists of two fast plastic scintillators combined with photomultiplier tubes, constant fraction differential discriminators (CFDD), a nanosecond delay, a multi-channel analyzer (MCA), and a time-to-amplitude converter (TAC)

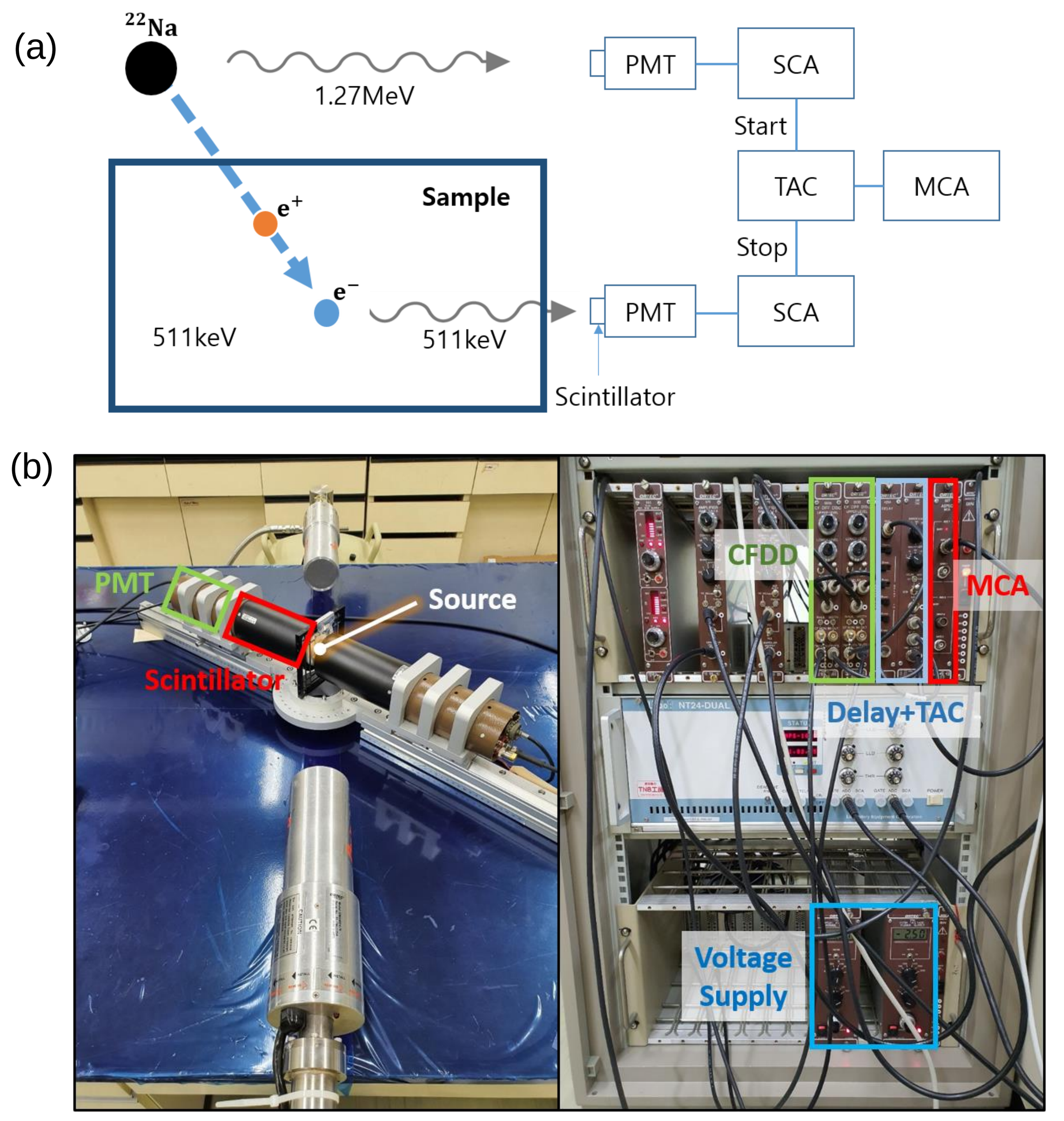

Fig. 1. (a) Block diagram of PALS system configuration and (b) measurement experiments setup

❖ Positron-Source/Sample Configuration

- Three commercially available proton exchange membranes (G, NR-211, NR-212) with different thickness (15 µm, 25 µm, and 50 µm respectively) were cut into 10 mm × 10 mm pieces
- Polymer pieces were stacked into 2 mm thickness on each side to prevent positron from escaping interest volume.

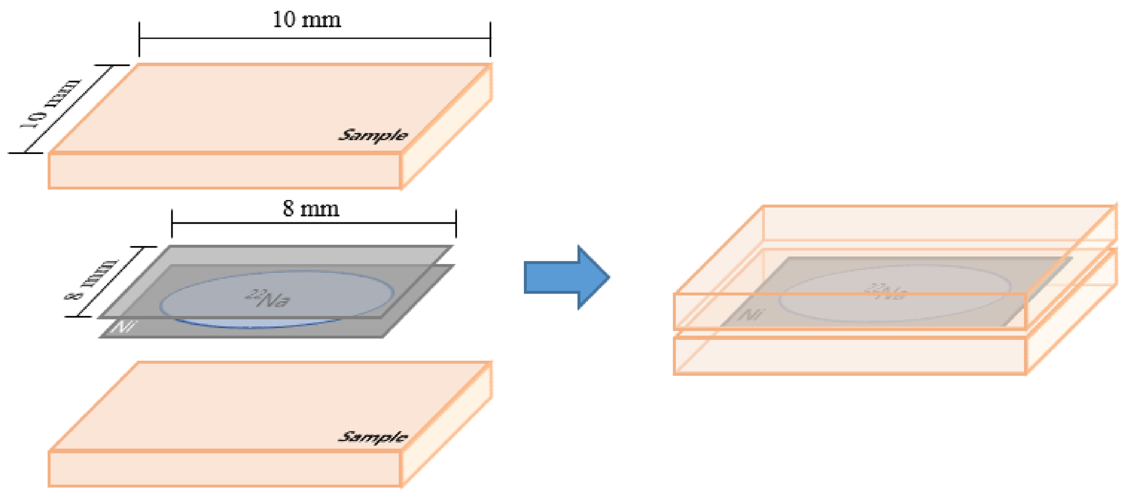

Fig. 2. Positron source/sample configuration (sandwich geometry)

Results

❖ Positron Annihilation Lifetime Spectra Fitting

- More than a million count was collected for each measurement and then analyzed by PALSfit3 software [4].
- The PAL spectra were decomposed into three lifetime components as shown in Fig. 2
- For polymer spectra, the third long-lived component indicates ortho-positronium (*o*-Ps) characteristic, or more specifically the *o*-Ps lifetime (τ_{o-Ps}).

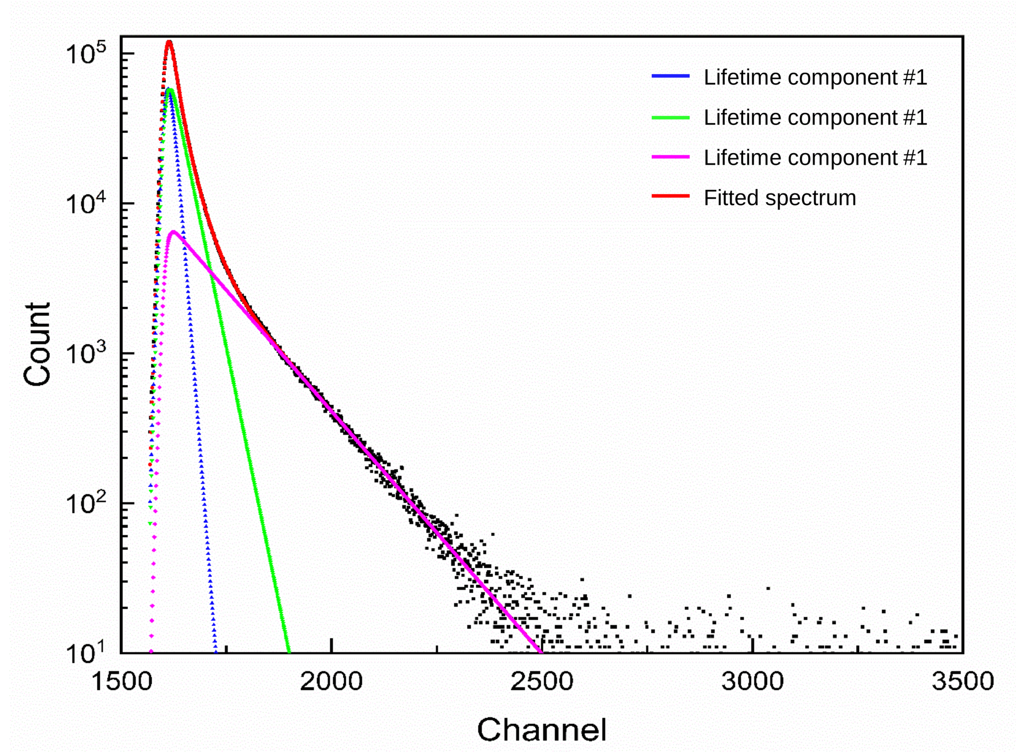

Fig. 2. The PAL spectrum fitting with PALSfit3 software[4]

- The reduced-χ^2 is equal to χ^2 divided by the degree of freedom (ν) of the curve-fitting problem.

❖ Free Volume Calculation

- Free volume size was calculated from Tao-Eldrup model and with the spherical approximation [5]

$$\tau_{o-Ps} = 0.5\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} (ns) \qquad V_f = \frac{4\pi R^3}{3}$$

R: radius of the spherical free volume. ΔR: 0.166 nm, the minimum thickness of the homogeneous electron layer overlapping with the positron wave function.

Table. 1. o-Ps lifetime (τ_{o-Ps}), o-Ps intensity (I_{o-Ps}), reduced-χ^2, and free volume size of proton exchange membranes

	τ_{o-Ps} (ns)	$I_{o-Ps}(\%)$	χ^2/ν	V_f (nm^3)
G (15μm)	2.4119	10.85	2.010	0.1381
NR-211 (25μm)	2.5703	10.57	1.279	0.1546
NR-212 (50μm)	1.6601	17.06	1.571	0.0671

Conclusion

- The Nafion free volume characterization by the KAERI PALS system was conducted.
- From the strong positive correlation of proton conductivity and free volume size, membranes with thickness less than 25 µm is desirable for PEMFC

Reference

1. S. Srinivasan, "Fuel Cells; From Fundamentals to Applications", Springer, Heidelberg, 2006
2. W. G. Grot, Perfluorinated ion exchange polymers and their use in research and industry, Macromolecular Symposia, Vol. 82, p 161-172, 1994.
3. H. F.M. Mohamed, E.E. Abdel-Hady, M.O. Abdel-Hamed, M. Said, Microstructure Characterization of Nafion HP JP as a Proton Exchange Membrane for Fuel Cell: Positron Annihilation Study, Acta Physica Polonica A, Vol 132, p1543-1547, 2017
4. P. Kirkegaard, J. V. Olsen, M. M. Eldrup, "PALSfit2: A software package for analyzing positron lifetime spectra", Technical University of Denmark, 2017
5. M. Eldrup, D. Lightbody, J. N. Sherwood, The temperature dependence of positron lifetimes in solid pivalic acid, Chemical Physics, Vol. 63, p51-58, 1981
6. T. Miyamoto, K. Shibayama, Free-volume model for ionic conductivity in polymers, Journal of Applied Physics, Vol.44, p5372, 1973