Transactions of the Korean Nuclear Society Virtual spring Meeting
May 13-14, 2021

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

Junyoung Lee [a,b], Jaegi Lee [a*], Young Su Jeong [a], Young Rang Uhm [a], Gwang-Min Sun [a], Sung-Joon Ye [b]
[a]*HANARO Utilization Division, KAERI, 111 Daedeok-daero 989beon-gil, Daejeon, 34057*
[b]*Program in Biomedical Radiation Sciences, Department of Transdisciplinary Studies, Graduate School of Convergence Science and Technology, Seoul National University, Seoul, 08826*
[*]*Corresponding author: jgl@kaeri.re.kr*

1. 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.

2. Methods and Results

2.1 System Setup

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).

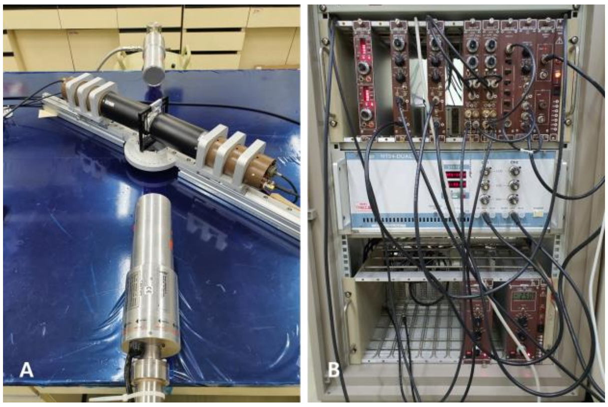

Fig. 1. A) Radioisotope source and scintillation detectors (black) and B) CFDDs, a nanosecond delay, an MCA, and a TAC embedded in nuclear instrumentation module (NIM) bin.

A 30 μCi $^{22}NaCl$ solution was deposited and evaporated on 2.5 μm thick nickel foils. The source and nickel foils were then sandwiched between the sample membranes.

2.2 Experimental Result

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 and were stacked.

More than a million count was collected for each measurement and then analyzed by PALSfit3 [4] software. 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 ($\tau_{o-\mathrm{Ps}}$).

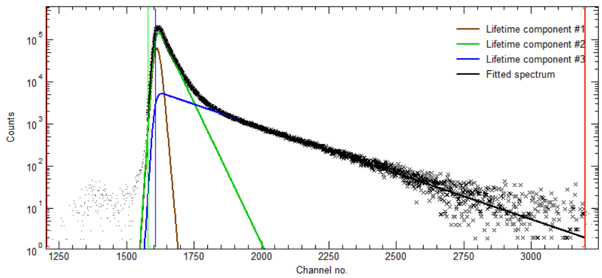

Fig. 2. The PAL spectrum fitting with PALSfit3 software [4].

Free volume size was calculated from $\tau_{o-\mathrm{Ps}}$ by Tao-Eldrup model and with the spherical approximation [5, 6]. The model equation is given as,

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

where R is the radius of the spherical free volume and $\Delta R = 0.166$ nm is the minimum thickness of the homogeneous electron layer overlapping with the positron wave function. The free volume size V_f can be calculated from the following equation,

$$V_f = \frac{4\pi R^3}{3} \qquad (2)$$

Table I summarizes key parameters of PALS free volume characterization. The reduced-χ^2 is equal to χ^2 divided by the degree of freedom (ν) of the curve-fitting problem.

Table I: *o*-Ps lifetime ($\tau_{o-\mathrm{Ps}}$), reduced-χ^2, and free volume size of Nafion membranes

	$\tau_{o-\mathrm{Ps}}$ (ns)	χ^2/ν	V_f (nm^3)
G $(15\mu m)$	2.4119	2.010	0.1381
NR-211 $(25\mu m)$	2.5703	1.279	0.1546
NR-212 $(50\mu m)$	1.6601	1.571	0.0671

3. Conclusions

The Nafion free volume characterization by the KAERI PALS system was conducted. The NR-212 showed the shortest *o*-Ps lifetime and, therefore, the smallest free volume. If the proton conductivity is the only concern, the strong positive correlation of proton conductivity [7] indicates that proton exchange membranes with thickness less than 25 μm is desirable for PEMFC.

Acknowledgment

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2017M2A2A6A05018529).

REFERENCES

[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 Unversity of Denmark, 2017
[5] S. J. Tao, Positronium Annihilation in Molecular Substances, The Journal of Chemical Physics, Vol.56, p5499, 1972
[6] M. Eldrup, D. Lightbody, J. N. Sherwood, The temperature dependence of positron lifetimes in solid pivalic acid, Chemical Physics, Vol. 63, p51-58, 1981
[7] T. Miyamoto, K. Shibayama, Free-volume model for ionic conductivity in polymers, Journal of Applied Physics, Vol.44, p5372, 1973