Low energy positron annihilation study of composite reverse osmosis membranes

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Abstract. Positron annihilation with a slow positron beam was applied to the characterization of composite reverse osmosis membranes. The results, obtained at different positron incident energies, indicated that the membranes are asymmetric with respect to the pore structure, consisting of a thin top layer with little porosity and an underlying thick porous layer. A relationship between the longest positron lifetime near the membrane surface and the salt rejection rate was discussed in terms of the free-volume hole size for the thin top layer.

1. Introduction

Reverse osmosis (RO) membranes have been applied to the separation of various substances for water purification and chemical waste treatment. In a separation process using a RO membrane, pressurized water containing dissolved salts contacts the feed side of the membrane, and water is taken out with depletion of salt concentration on the other side. Separation of salts with RO membranes is considered to relate to molecular-level holes in the membranes, thus deeper knowledge with respect to the hole structure allows prediction of better membrane performance. Positron annihilation (PA) is known as a powerful tool for examining the hole structure of functional materials at a molecular level. [1-3]

In vacuum, ortho-positronium ($o$-Ps), a hydrogen-like triplet positron-electron pair, annihilates into 3γ rays with an intrinsic lifetime of 142 ns. If $o$-Ps is localized in a molecular-size hole, it annihilates with a lifetime much shorter than 142 ns through a 2γ pick-off process upon a collision with an electron at the hole wall. The $o$-Ps lifetime is documented to be well correlated with the hole dimension [4]. In addition, confinement of $o$-Ps to a smaller hole (especially sub-nm size) reduces more the probability of 3γ annihilation, a complementary process to 2γ annihilation. This enables one to analyze the layer structure of the composite membranes based on the 3γ annihilation probability observed with a variation of the positron incident energy [5-6].

In this work, PA with a variable-energy positron beam was applied to the characterization of the hole structure for the composite RO membranes, consisting of a thin top layer and an underlying thick substrate. We report results on the hole structure of RO membranes with different chemical structures of the top layers, obtained by using positron annihilation techniques, and discuss the positron results, in comparison with the salt rejection performances.
2. Experimental
Two kinds of commercially-available membranes (NTR729HF and LF10) were supplied by NITTO DENKO Corp., Japan. Both of them were obtained as composite membranes of polyvinyl alcohol and polyamide fabricated on polysulfone substrates through interfacial polymerization.

Positron annihilation γ-ray spectra were measured with a $^{22}\text{Na}$ source based, magnetically guided positron beam[7]. The fraction of $3\gamma$ decay annihilation was determined from the relative fraction of $3\gamma$ annihilation with energies lower than the 511-keV photo peak in the positron annihilation spectra observed at an incident energy between 0 and 10 keV. An intense pulsed-positron beam generated with an electron linear accelerator at AIST, was utilized for measuring lifetimes of positrons with an incident energy of 1.0 keV [8]. The recorded positron lifetime data were analyzed assuming three exponential components to deduce the average lifetime and relative intensity of $o$-Ps.

3. Results and Discussion
3.1. Positron annihilation γ-ray spectroscopy
Figure 1 shows the fraction of $3\gamma$ annihilation, $f_{3\gamma}$, as a function of positron incident energy for the RO membranes. For LF10, $f_{3\gamma}$ decreases with increasing incident energy from 0.6 keV to 1.0 keV. In the range of the incident energies from 1.0 keV to 2.5 keV, $f_{3\gamma}$ goes to a minimum value, meaning most $o$-Ps undergo $2\gamma$ annihilation at these incident energies. With further increasing the incident energy from 2.5 keV to approximately 5.0 keV, $f_{3\gamma}$ rises significantly, and then above 5.0 keV, LF10 membrane exhibits a flat stage in $f_{3\gamma}$ at these higher incident energies. As for NTR729HF, the lowest $f_{3\gamma}$ is observed in the energy range from 0.6 keV to 1.0 keV. With continued increase of the incident energy, $f_{3\gamma}$ increases dramatically. Fairly large $f_{3\gamma}$ are observed at the incident energies higher than 3.5 keV.

![Figure 1. The fraction of 3γ annihilation $f_{3\gamma}$ as a function of incident energy for reverse osmosis membranes with different composition.](image)

The slight increase of $f_{3\gamma}$ with reducing the incident energies below 1.0 keV for LF10 indicates some $o$-Ps formed near the surface, may escape out from the membrane, and self-annihilate in vacuum. With the increase of the incident energy, less $o$-Ps can escape out from the membrane, which results in the reduction of $f_{3\gamma}$. For both membranes, the lowest $f_{3\gamma}$, observed around an incident energy of 1.0 keV, indicates that most positrons undergo $2\gamma$ annihilation at corresponding depth in the membranes. Since $3\gamma$ annihilation occurs only when $o$-Ps exists in vacuum or in relatively large pores, the lowest $f_{3\gamma}$ indicates that most positrons annihilate in a pore-free layer at these incident energies and the higher $f_{3\gamma}$ indicates some positrons annihilate in a porous one. Thus the obtained results signify that most positrons annihilate in the dense top layer at the energies range from 1.0 keV to 2.5 keV and 0.6
keV to 1.0 keV for LF10 and NTR729HF, respectively, and both RO membranes have porous substrates, which leads to the higher $3\gamma$ annihilation at the incident energy higher than 3.0 keV.

3.2. Positron annihilation lifetime measurements and membrane performance

As seen in Figure 1, NTR729HF and LF10 membranes exhibit the lowest fraction of $3\gamma$ decay at the incident energies around 1.0 keV. This means in this energy range most positrons annihilate in the dense top layer, responsible for the separation. Therefore, we collected the positron lifetime data at the incident energy of 1.0 keV to investigate the free volume holes in the top layer for the RO membranes as well as to compare the lifetime data with the separation performance.

Figure 2 displays the raw positron lifetime data for the RO membranes acquired at an incident energy of 1.0 keV. A spectrum for Kapton which has no long-lived lifetime component is also shown for comparison. The difference in the slopes around 5 ns indicates that two RO membranes have free-volume holes with different sizes. Weak satellite peaks appear on the tail of the lifetime data, which may be due to the bunching of some unchopped slow positrons. In our measurements using a positron pulsing system, positrons from the accelerator are chopped with 20 MHz and further bunched into narrow-width pulses with a frequency higher than 20 MHz. During the data accumulation, a small number of unchopped positrons may be bunched continuously, resulting in the background with a time structure. To take into account this effect at analysis, lifetime data for Kapton were used as a background reference. The recorded data were confirmed to be well resolved into three lifetime components with a reasonable variance of fit.

![Figure 2](image)

**Figure 2.** The positron lifetime data recorded with an incident energy of 1.0 keV for reverse osmosis membranes with different composition and Kapton reference.

| Membrane       | $\tau_3$ (ns) | $I_3$ (%) | Free volume hole size (nm) | NaCl rejection (%) |
|----------------|---------------|-----------|---------------------------|-------------------|
| LF10           | 1.32          | 23.6      | 0.21                      | 99.5              |
| NTR729HF       | 2.12          | 14.9      | 0.30                      | 75.0              |

**Table 1.** Average lifetime $\tau_3$ and relative intensity $I_3$ of $\sigma$-Ps, free-volume hole size, and NaCl rejection for the composite RO membranes

From the obtained $\sigma$-Ps lifetimes, the free-volume hole sizes of the top layers were calculated based on the Tao-Eldrup model [9,10], and are presented in Table 1 with the average lifetime $\tau_3$ and relative intensity $I_3$ of $\sigma$-Ps. The free-volume hole sizes in the top layer of NTR729HF and LF10 are 0.30 nm.
and 0.21 nm, respectively, and the hole of the former membrane is found about 1.5 times larger than the latter.

The most important indicator of the separation membrane performance is the rejection of specified salts. The desalination by RO membrane is normally explained in terms of Donnan and/or size exclusion effects. If the holes involved in the separation process are far smaller than a target salt, the transportation of the salt ions would be effectively restrained. In Table 1, the values of NaCl rejection for both membranes are also listed, which shows the separation performance of LF10 is much higher than NTR729HF. This result is consistent with the quantified hole sizes in the top layer of the two membranes, that is, LF10 with a smaller free-volume prevents salt ions more than NTR729HF.

4. Summary

The low-energy positron annihilation techniques have been applied to the characterization of the composite RO membranes of LF10 and NTR729HF. The obtained results suggested that both the membranes consist of a dense surface top layer on a porous substrate and an important role in the separation performance is played by the free volume sizes in the top layer. A combined use of the low-energy positron annihilation lifetime and γ-ray techniques was demonstrated to be useful for examining the hole structure of reverse osmosis membranes.

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