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Depth profiling of the free-volume holes in cellulose triacetate hollow-fiber membranes for reverse osmosis by means of variable-energy positron annihilation lifetime spectroscopy

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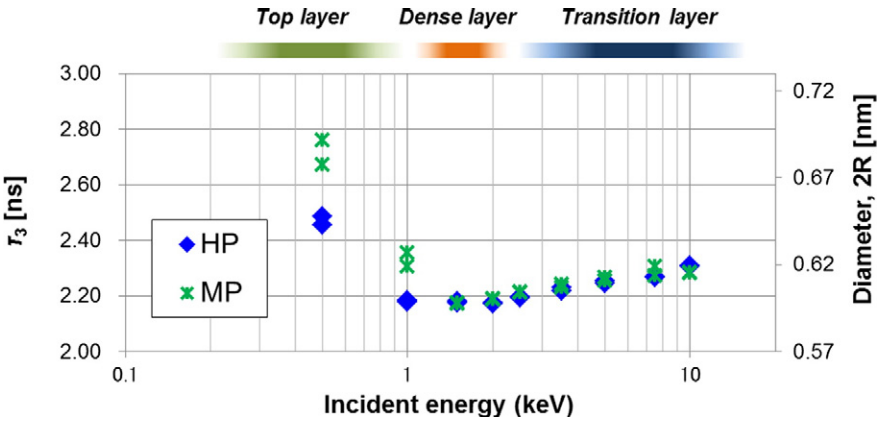
HIGHLIGHTS

- CTA hollow-fibers were studied by the energy-tunable positron annihilation.
- The free-volume hole size was quantified from the long-lived positronium lifetime.
- The dense-layer was determined from the depth profile of the free-volume hole.
- The dense-layer thickness was found to be correlated with the water flux.

GRAPHICAL ABSTRACT



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ABSTRACT

Two types of commercial cellulose triacetate hollow-fiber membranes with different water fluxes, apposite for a reverse osmosis separation process, were investigated by means of positron annihilation lifetime spectroscopy with a ^{22}Na-radioisotope-based energy-tunable positron beam, in order to elucidate a depth profile of the free-volume hole size in a subnanoscopic viewpoint. The lifetimes of *ortho*-positronium (*o*-Ps), the triplet positron-electron pair, for the two membranes were measured as a function of positron incident energy *E*. The *E* dependence of the hole size, quantified from the *o*-Ps lifetime, indicated that the separation-active dense layers with the smallest hole sizes are located at the near-surface region for both the membranes. The ratio of the dense-layer thicknesses for the two membranes was estimated to be more than 50% of the ratio of the respective effective thicknesses calculated from the water flux based on Darcy's law. The result signified that the dense layer with the smallest hole size at the near-surface region considerably contributes to the difference in the water flux.

1. Introduction

Improving the water flux of hollow-fiber membranes is a key issue to develop an innovative material with higher operation efficiency for reverse osmosis (RO) processes. The flux closely associates with the membrane thickness according to molecular-transport

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models [1,2]. Hence, for developing novel separation membranes with asymmetric structure, controlling their layer structure is of importance to attain superior water flux along with higher separation ability. Scanning electron microscopy is a useful tool to characterize the porous layer structure for those membranes in a micrometer or nanometer scale. For further clarification of the water transport mechanism related to the total flux for the separation membranes, it is necessary to characterize the near-surface layer structure from the *subnanoscopic* viewpoint.

Energy-tunable positron annihilation lifetime spectroscopy (PALS) is a unique method to elucidate the depth profile of subnanoscopic free volumes existing in the near-surface region of polymeric separation membranes. The technique has been proved to be useful for characterizing the free-volume holes relevant to the ion separation for polymeric membranes [3–8]. In PALS, the lifetime of *ortho*-positronium (*o*-Ps), the triplet bound state of a positron and an electron, is measured to evaluate the size of free-volume holes in a material. Chen et al. demonstrated that the free-volume hole sizes, quantified from the *o*-Ps lifetimes, are well correlated with the separation ability of polymeric composite membranes for water purification [5].

In this work, we investigated the depth profile of the nanoscopic free volumes for commercial cellulose triacetate (CTA) hollow-fiber membranes, applicable to the RO process, by means of PALS with a ^{22}Na-radioisotope-based energy-tunable beam, in order to identify the separation-active layer of the present asymmetric membranes with respect to the free-volume size. The relationship between the water flux and the active-layer thickness, possibly relevant to the water molecule transport, is discussed.

2. Principle

Some of the positrons, introduced into insulating materials such as organic polymers, may form either *o*-Ps or *para*-positronium (*p*-Ps), the singlet state of Ps. In vacuum, *o*-Ps annihilates into 3γ rays with an intrinsic lifetime of 142 ns, while *p*-Ps annihilates into 2γ rays with an intrinsic lifetime of 125 ps. When *o*-Ps forms in a substance, it tends to localize in intermolecular spaces like free-volume holes in a polymer, and annihilates with a lifetime shorter than 142 ns, typically a few ns, through a 2γ pick-off process upon a collision with an electron belonging to the surrounding molecules. Consequently the lifetime of *o*-Ps, annihilated in a hole, is well correlated with the hole dimension. The relationship between *o*-Ps lifetime τ [ns] and radius R [nm] of a spherical hole is expressed based on the Tao–Eldrup model as follows, [9–12]

$$\tau = 0.5\left[1-\frac{R}{R+0.166}+\frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+0.166}\right)\right]^{-1}. \quad (1)$$

A variable energy positron beam provides the depth-profiling ability to PALS. One can control an implantation depth of positrons from the sample surface through tuning their incident energy E. The trajectory distance of the positrons depends on E and density ρ, so that the correlation between E [keV] and the mean implantation depth of the positrons Z_m [nm] is expressed by the following equation, [3,12]

$$Z_m = \left(\frac{40}{\rho}\right)E^{1.6} \quad (2)$$

where the unit of ρ is g/cm^3.

3. Experiments

3.1. Sample

Two kinds of CTA hollow fibers, high-pressure (HP) and medium-pressure (MP) operative membranes adapted for the HOLLOSEP® modules, were supplied from TOYOBO, Japan as stored in water. The HP and MP fibers were taken out from commercial modules, HR5255 (ϕ153 mm × 825 mm) and HA5230 (ϕ150 mm × 840 mm), respectively. The outer and inner diameters of both the hollow fibers were about 100 μm and 40 μm, respectively. Their separation performance and testing conditions are summarized in Table 1. Note that the deduced water flux for HP (0.74 L/(m^2 h MPa)) is more than four times as small as that for MP (3.42 L/(m^2 h MPa)), while the NaCl rejection of both the membranes is high, that is, 99.6% and 94% for HP and MP, respectively. Before the PALS measurements, the membranes were washed by soaking in ion-exchanged water for 1 day and then were dried in air for more than 2 days. The measurement samples were prepared by tightly placing the numerous fibers in parallel on a square of Kapton® film with a size of 15 mm × 15 mm so that all positrons with a beam diameter of several millimeters are irradiated on the membrane surface.

3.2. PALS measurements

PALS measurements were carried out at various positron incident energies, E, ranging from 0.5 keV to 10 keV using a ^{22}Na-based pulsed positron lifetime measurement system (PALS200A, Fuji-Imvac, Japan). A schematic diagram of PALS200A is shown Fig. 1. The time resolution for the measurement system was approximately 290 ps full-width half-maximum. The lifetimes of positrons were recorded as the time difference between a pulsing trigger and the corresponding detection timing of the annihilation radiation from the sample, and the annihilation events were accumulated with 2.0 million counts for each sample. The measurement at each E was performed twice at room temperature. Multi-exponential analysis by using the RESOLUTION fit was applied to the recorded lifetime data to calculate the average lifetime of *o*-Ps τ_3 as the third component for the present membranes. In the analysis, care was taken of the background component for the lifetime data by using Kapton® data with 3.0 million counts.

4. Results and discussion

Typical results of the positron annihilation lifetime data at E = 1.0 keV for the MP and HP membranes are shown in Fig. 2 with Kapton reference data. In comparison with the reference, both the data for the membranes clearly display a long-lived lifetime component due to the *o*-Ps pick-off annihilation in the free-volume holes. Fig. 3 shows the

Table 1
Separation performances and testing conditions for the cellulose triacetate hollow-fiber membranes.

Sample ID	NaCl rejection [%]	Operating pressure, p_o [MPa]	Osmotic pressure, p_l [MPa]	Product flow rate, P [m^3/day]	Surface area, A [m^2]	Applied pressure, p_o–p_l [MPa]	Water flux, J [L/(m^2 h MPa)]
HP	99.6	5.39	2.97	3.0	70	2.42	0.74
MP	94.0	2.94	0.13	15.0	65	2.81	3.42

The NaCl rejection, p_o, P and A, provided for the respective modules from the manufacturer, are nominal values determined at 25 °C with the conditions of NaCl concentrations 35,000 mg/L and 1500 mg/L for HP and MP, respectively. p_l and J were calculated from the NaCl concentration and P with A and the applied pressure, respectively.