Performance evaluation of polyamide TFC membranes: Effects of free volume properties on boron transport

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ARTICLE INFO

ABSTRACT

To comprehensively investigate the correlation between free volume properties (size and distribution) in the interior of polyamide (PA) active layer and mass transport mechanism, six polyamide thin film composite (TFC) membranes were characterized using positron annihilation lifetime spectroscopy (PALS). In case of pressurized filtration conditions, the rejection rate of boron across all PA membranes was found to be inversely proportional to the free volume size. The more boron transport occurred at the membrane containing larger free volume. In addition, the transition of the neutral boron transport mechanism from convection to diffusion was found to occur at a membrane free volume radius around 0.275 nm within the applied pressure range (2 and 10 bar), as verified by PALS and the dimensionless Peclet number. We believe that mass transport mechanism transition from convection to diffusion is caused by the compression of polyamide active layer due to applied hydraulic pressure (10 bar), resulting in lowering the convective mass transport pathway inside polyamide active layer. These membrane free volume size criteria and experimental filtration results may subsequently be used as new design guidelines for the development of high boron rejection polyamide TFC membranes having a low energy consumption.

1. Introduction

Generally, solute transport mechanisms are known to be closely related to the pore size. The size of the membrane pore, expressed as the length or molecular weight cut-off (MWCO), has widely been used as core criteria for categorizing the water-treatment membranes, such as nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO) membranes. Depending on the size and permanence of membrane pores, membranes that have a mean pore size larger than 1.0 nm follow a convective transport mechanism (pore-flow), whereas membranes having atomic-scale pores smaller than 0.5 nm can be operated under diffusion dominant conditions (solution-diffusion) [1,2]. It was widely reported that the transition of solute transport mechanisms can happen at the intermediate region (pore diameter ranging from 0.5 to 1.0 nm).

This range of pore size is also used to distinguish between NF and RO membranes, considering the membrane and solute properties. In recent studies into carbon-based inorganic membranes consisting of carbon nanotubes (CNTs) and graphene, there is another perspective for the porosity of active layer, i.e., nanoporosity [3,4]. In these publications, the authors assume that pores smaller than 1.0 nm are nanopores and that the pore size can be controlled by replacing the chemical binding near the nanopore. In addition, only a sieving mechanism was considered in these carbon-based membranes. Despite various previous researches about the porosity of ion-rejecting active layer, however, actual mechanism transition of solute transport through a thin active layer containing a free volume in this pore size range has remained relatively unknown to date.

Since the 1980s (after intense controversy of mass transport

mechanisms), the active layer of salt-rejecting membranes has been regarded as non-porous in nature. In the solution-diffusion model, it was believed that solutes are separated based on differences in the solubility and diffusivity of solutes within the non-porous active layer [2]. However, the presence of a free volume and cavities inside the polyamide active layer has been confirmed via various analytical techniques, and that they perform roles analogous to membrane pores even though they are not interconnected inside the active layer [5–7]. Despite this situation, almost all membrane researchers still follow the solution-diffusion model to simulate the mass transport of polyamide TFC membranes due to their simplicity. However, this discordance of standards for pore size and solute transport across a thin active layer could lead to misunderstandings regarding the transport phenomena and the manufacturing of poor membrane processes having a low solute removal efficiency, resulting in potentially severe spills of harmful solutes such as boron and micropollutants. Therefore, there is a huge need to re-evaluate and develop accurate standards regarding mass transport across a thin active layer for highly efficient membrane processes.

To comprehensively understand solute transport mechanisms across a thin polyamide active layer, various analyses related to the pore (free volume), charge and hydrophobicity of the membrane, and membrane performance are simultaneously required [8]. Due to recent advances in several positron technologies using positron annihilation phenomena, the atomic-scale voids or free volumes inside polyamide active layers have been correctly estimated using positron annihilation lifetime spectroscopy (PALS) [9,10]. To date, the characterization of free volume size and intensity inside the polyamide active layers by PALS has been frequently demonstrated [5,6,9,11,12]. Since most incident positrons may be annihilated within the active layer thickness (20–200 nm) at a 1–2 keV incident positron—a common range in PALS studies [6,12–17]—the positron lifetime and intensity reveal information about the free volume or cavities inside the active layer [18].

In most PALS research, the influence of several variations (i.e., control of polymer concentration, addition of hydrophilic additives, heat treatment, etc.) on the free volume properties of polyamide active layer have mainly been studied to improve the membrane performance (water flux and solute rejection) [5,16,17,19]. As well as dry membrane, free volume properties of wet membrane were also analyzed by PALS to assess the swelling properties of polyamide active layer [20,21]. From the review of previous PALS research, free volume diameters measured by PALS for polyamide TFC membranes such as NF, RO, and FO membranes ranged from 0.40–0.78 nm, which potentially overlaps with the mass transport transition region (0.5–1.0 nm) from diffusion to convection. Nevertheless, no comprehensive mass transport research using PALS results has been reported to date. To the author's knowledge, this is the first paper to use pore size and distribution results obtained by PALS to evaluate the mass transport mechanism of polyamide TFC membranes.

Therefore, the objectives of this study are to evaluate several physicochemical properties including free volume size and intensity of polyamide membranes using PALS, and to then exploit this information for the verification of the transport mechanism transition and correlation between boron transport mechanism and free volume properties. A slow positron system was utilized to characterize the free volume size and intensity at diverse penetration depths. Evaluations of basic membrane properties and performances were also carried out in pressure-driven and osmosis-driven filtration units. To minimize the effects caused by hydrophobicity and surface charge of polyamide active layer closely related to the solute rejection, boron was chosen as the model solute and rejection experiments were carried out at a neutral pH [22,23]. Finally, a theoretical reconfirmation of boron transport was performed based on the calculation of a dimensionless Peclet number using rejection experiment results to investigate the actual assessment of the mass transport mechanism that occurred inside the polyamide active layer.

2. Experimental

2.1. Membranes and chemicals

Among various ion-rejection membranes, ranging from nanofiltration to forward osmosis membranes, six polymeric membranes comprising a thin polyamide active layer were selected to elucidate mass transport phenomena that depend on the properties of a polyamide active layer. The membranes were denoted as NF1, NF2, RO1, RO2, FO1, and FO2. From the manufacturers, basic information of each membrane about the water flux and solute rejection are summarized in Table S.1. All membranes were washed with de-ionized water several times and stored at 4 °C before use.

NaCl, $MgSO_4$, and boron were used for the rejection experiments and forward osmosis tests. Boron solutions were prepared from concentrated stock solutions of boric acid (H_3BO_3, SHOWA, Japan). De-ionized water having a resistivity of 18.2 MΩ cm supplied from a Milli-Q water purification system (Elix 5, Merck Millipore Corporation, Germany) was used throughout this study unless stated otherwise.

2.2. Physicochemical characterization of polyamide membranes

To observe the surface morphology and roughness of the polyamide membranes, microscopic analysis tools such as scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed, as described in our previous study [24]. To obtain the clear cross-section images for SEM, liquid nitrogen and sharp razor blade were used. Overall membrane thickness, including the active layer and support layer, were measured using stylus profilometry (DekTak XT, Bruker Corporation, USA). To evaluate the hydrophobicity of both membrane surfaces, a contact angle goniometer (Phoenix-300 Touch, Surface Electro Optics Co., Ltd., Korea) was used based on the captive bubble method. To ensure experimental accuracy, five-time measurements were carried out for each sample. In addition, a vacuum oven and electronic balance were used to determine the porosity of the polyamide membranes according to the method reported by Zheng et al. [25]. Mechanical properties such as tensile strength, Young's modulus, and strain at break were determined using an Advanced Materials Testing System (LS1, Lloyd Instruments Ltd., UK). The gauge width and crosshead speed were 10 mm and 10 mm/min, respectively. In all experiments, except for the porosity measurement, dried membrane samples kept overnight in a desiccator were used, and all membranes samples were randomly selected from a large sheet of each polyamide membrane.

2.3. Surface charge and chemical composition of polyamide active layer

To systematically investigate the mass transport behaviors across the active layer of polyamide membranes, the surface charge and chemical composition of the polyamide active layer were examined. A zeta potential analyzer (ELS-Z, Otsuka Electronics, Japan) was used to examine the surface charge of the polyamide active layer via the streaming potential method. To estimate the isoelectric point of polyamide layer, 10 mM NaCl electrolyte solutions at pH 4, 7, and 10 were consecutively used. For functional group characterization, a Fourier transform infrared (FT-IR) spectrometer (Cary 660, Agilent, USA) was employed. The absorbance spectra from 800 cm^{-1} to 1800 cm^{-1} were acquired at a 4 cm^{-1} spectral resolution, and peaks indicating amide I, II, and polysulfone functional groups were subsequently selected to calculate the intensity ratio. In addition, X-ray photoelectron spectroscopy (XPS) was carried out using a VG Microtech MultiLab ESCA 2000 (Thermo VG Scientific, UK) with Al K-alpha software to examine the chemical composition of the active layer. The dried membrane samples were scanned from a 0 eV to 1200 eV binding energy at 0.5 eV steps. Based on the elemental composition (C, O, N) of the active layer, the cross-linking density of polyamide active layer were estimated using the