The porous structure of the fully-aromatic polyamide film in reverse osmosis membranes

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ABSTRACT

In this study, the porous structures of two commercial fully-aromatic polyamide (FAPA) reverse osmosis (RO) membranes as well as homemade RO membranes were thoroughly characterized and revealed by using SEM and TEM. With a designed "inverse" interfacial polymerization experiment, it was confirmed that pores always form on the surface of the FAPA film facing the aqueous phase. Based on the SEM observation on the cross-section of FAPA film and the TEM results, a new structure model of FAPA film in RO membrane was proposed. The dense layer of the flat area and the dense layer near the top surface of the protuberances and ridges connect together to form a complete dense discriminating layer as the key barrier layer of the RO membrane. Protuberances and ridges have irregular interconnecting cavities and tunnels, through which the dense layer and the pores on the back surface of the FAPA film are connected. All these findings proved the correctness of Cadotte's assumption about the pores' forming mechanism during interfacial polymerization process.

1. Introduction

Reverse osmosis (RO) technology is one of the most important technologies for providing sustainable water supplies. State-of-the-art commercial RO membranes utilize a thin film composite design consisting of a fully-aromatic polyamide (FAPA) selective film on a porous polysulfone (PSF) support layer [1]. The FAPA film is typically formed via the interfacial polymerization (IP) of m-phenylenediamine (MPD) and trimesoyl chloride (TMC), which results in a rapid formation of a highly cross-linked network [2]. As many properties of RO membranes, such as permselectivity, resistance to oxidation properties, and fouling resistance are mainly determined by this cross-linked FAPA film [3–11], it is important to study its detailed structure for optimizing the RO membrane performance.

Mathematical models describing RO transport phenomena assume that water and solute permeation can be classified as solution-diffusion or pore-flow permeation mechanism. In solution-diffusion models [12,13], the FAPA film is considered nonporous, and water and solute permeation is the result of partitioning into and diffusion through the FAPA film. In pore-flow models [14–16], the FAPA film is considered porous, and permeation occurs through a combination of hindered diffusion, advection, and electromigration through pores. In recent years, some studies suggested that the structure of the FAPA film is asymmetric and a thin barrier layer exists in the FAPA film [17–20]. Freger predicted that a dense barrier layer would exist in the middle of the FAPA film with loose layers on both sides, and the dense layer was water-selective and much thinner than the superficial layer of the FAPA film [19]. Ghosh and Hoek also pointed out that rejection may occur at a dense inner barrier layer and the visible surface morphology is a byproduct of the IP process [20]. Some researchers from Nitto Denko and Toray reported the thickness of the dense layer without discussing its specific location in the FAPA film. For example, a research group from Nitto Denko reported that dense layers of 15–30 nm thick were found inside the FAPA film of their self-made RO membranes. The water flux of RO membranes would increase when a thinner dense layer was formed [21,22]. One patent from Toray disclosed that the thickness of the separation function layer for composite RO membrane was preferably between 14 and 22 nm [23]. This thickness range of composite RO membrane can maintain the balanced performance in flux and resistance to chemical cleaning.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the most commonly used imaging techniques for studying the microstructures of polyamide film of RO membranes. SEM was mostly used to characterize the surface, or more

accurately, the top-surface of the FAPA films, whose morphologies were usually described as ridge-and-valley [23–26] and protuberance structures [2,27]. The back surface of the polyamide film has seldom been studied, and there are only a few papers studying the back surface morphology using SEM [28–31]. By removing the polysulfone support with solvent, Lee et al. reported the porous structure on the back surface of the FAPA film of DOW SW30 RO membrane, and suggested that the pores would relate to the surface structure of the FAPA film [29]. TEM has been mostly used to investigate the cross-section structure of RO membranes [4,18,20–26]. Freger employed selective staining methods to identify the polyamide film within RO membrane, and reported that the overall thickness of the FAPA film was about 200–300 nm [18]. Kong et al. provided clear cross-section of TEM images of the polyamide film, which showed the protuberances on the surface of polyamide films were cavity-like inside [27]. In order to avoid artifacts that could be introduced by the dehydration step during TEM sample preparation, Pacheco et al. presented cross-section images of isolated polyamide thin films without the PSF support membrane [24]. Furthermore, they obtained the "projected area" TEM (PA-TEM) images by placing the surface of isolated FAPA films perpendicular to the TEM electron beam, and showed more details of the structures inside FAPA films.

Although the structure of the FAPA film in RO membranes has been extensively studied, up to now, there is still no clear description about its precise structure, especially the structure inside FAPA film. Some important structure information, such as the exact location of the key barrier layer, still remains controversial. To thoroughly characterize the detailed structure of FAPA films is still challenging due to the complexity and fragility of its nature. In this paper, we studied the detailed structure (top surface, back surface and cross-section) of the FAPA film in commercial RO membranes using SEM and PA-TEM. By designing an "inverse" IP procedure to fabricate FAPA film, we verified Cadotte's assumption about the pores' forming mechanism during IP process [2]. We found that the FAPA film has multi-level porous structures inside and provided a clear evidence of the exact location of the key barrier layer. We also proposed a new schematic model to reveal the whole structure of the FAPA film for the first time.

2. Experimental

2.1. Chemicals and materials

Two commercial composite RO membranes for brackish water filtration were examined in the current study (ESPA2 from Hydranautics, BW30 from Dow). Commercial PSF ultrafiltration membrane (PS-35 from Sepro) was used as the support membrane. MPD, TMC, triethylamine (TEA), and n-methyl-2-pyrrolidone (NMP) were purchased from Aldrich. Rhodamine B was purchased from Beijing Chemical Works. Isopar E solvent was purchased from ExxonMobil Chemical. All reagents were of analytical grade purity and were used as received without further purification.

2.2. FAPA film prepared via conventional IP procedure

Dry PSF support membrane PS-35 was first immersed in deionized water for 24 h, and then rolled with a rubber roller to remove excess water and mounted in a 20×20 cm^2 Teflon frame for IP reaction. 50 ml aqueous solution containing 2% (w/v) MPD and 1% (w/v) TEA was poured onto the PSF support membrane and kept for 1 min. The excess aqueous solution was removed with a rubber roller. Subsequently, 50 ml organic solution (isopar E) containing 0.1% (w/v) TMC was poured onto the membrane soaked with aqueous solution. After 1 min of IP reaction, the excess organic solution was drained, and the membrane was subsequently heat cured at 70 °C for

3 min. At last, the membrane was washed thoroughly with deionized water and stored in deionized water at 5 °C for later use.

2.3. FAPA film prepared via "inverse" IP procedure

Dry PSF support membrane PS-35 was first mounted in a 20×20 cm^2 Teflon frame for IP reaction. 50 ml organic solution containing 0.1% (w/v) TMC was poured onto the PSF support membrane, and kept for 1 min. Then the excess organic solution was poured and the membrane was dried in air for *ca.* 10 s to make sure the PSF support membrane was still coated with a thin layer of the organic solution. Subsequently, the support membrane with PSF layer facing down was immersed into an aqueous solution containing 2% (w/v) MPD and 1% (w/v) TEA. After 1 min of IP reaction, the membrane was slowly taken out of the aqueous solution and heat cured at 70 °C for 3 min. At last, the membrane was washed thoroughly with deionized water and stored in deionized water at 5 °C for later use.

2.4. Membrane characterization

Morphologies of the FAPA films on top surface, back surface and cross-section were observed using SEM. SEM images were collected using an S-4800 (HITACHI, Japan) at an accelerating voltage of 2 kV to minimize any damage by the electron beam. Samples were previously sputter-coated with a uniform layer of palladium to avoid charging effects.

To observe the back surface of the FAPA film, the nonwoven polyester backing was first peeled off. The rest RO membrane was placed on a steel mesh (mesh number: 400) with the PSF support membrane facing up, and then washed with NMP to thoroughly remove the PSF support membrane. The washing procedure with NMP was repeated for several times until there were no white precipitates visible. The sample on the steel mesh can be later observed in SEM after removing the residual NMP in a vacuum oven at 50 °C.

The RO samples for SEM cross-section investigation were prepared as follows: unused wet RO sample was cut into a ribbon shape and immersed in deionized water for 10 min. Then the wet RO sample was immediately put into liquid nitrogen and kept for 15 min before fracturing. The FAPA film and PSF layer can be easily fractured inside the liquid nitrogen with a pair of tweezers. Later when the samples returned to the room temperature, the polyester backing can be easily cut with scissors.

The structure inside FAPA films was studied using the PA-TEM method [24]. PA-TEM images were acquired with a FEI TH30 TEM at an accelerating voltage of 300 kV using Gatan CCD cameras. The samples preparation method were similar to the SEM samples for back surface observation, except that the FAPA films were transferred onto copper grids rather than steel meshes.

Permeate flux and salt rejection of the RO membranes were tested by standard cross-flow permeation tests. The filtration apparatus employed was a stainless cell (CF042SS, Sterlitech Corp.) with an active filtration area of 42 cm² and was operated at a pressure of 1.5 MPa at a cross-flow velocity of 0.35 m/s. The feed solution is 2000 ppm NaCl aqueous solution, and a cooling system is used to control the temperature of feed solution at 25 °C. The pH of the feed solution is not adjusted and is around 6.0. The electric conductivities of the feed and permeate solutions were measured using a conductivity meter (Cond 3310 WTW). Rejection and permeate flux were calculated using the following equations:

Permeate flux; $J = (\Delta v / \Delta t \times s)$

Salt rejection; $R = 1 - (c_p / c_f)$ where Δv is the permeate volume, Δt is the permeation time, and s is the effective membrane area. c_p is the permeate concentration and c_f is the feed concentration.