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## Investigating the void structure of the polyamide active layers of thin-film composite membranes

Lin Lin<sup>a</sup>, Rene Lopez<sup>b</sup>, Guy Z. Ramon<sup>c</sup>, Orlando Coronell<sup>a,\*</sup><sup>a</sup> Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-7431, United States<sup>b</sup> Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3255, United States<sup>c</sup> Department of Civil and Environmental Engineering, Technion – Israel Institute of Technology, Technion City, Haifa, Israel

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## ABSTRACT

The potential presence of voids in the fully-aromatic polyamide active layers of thin-film composite (TFC) membranes for water purification was studied in a selection of commercial membranes with a broad range of performance levels. The membranes were characterized for their potential void fractions using three independent methods: (i) analysis of transmission electron microscopy (TEM) images of membrane cross-sections, (ii) water uptake measurements by quartz crystal microbalance (QCM), and (iii) estimates of the effective refractive indices of active layers by spectroscopic ellipsometry. Results revealed that voids having tens of nanometers in diameter exist in the fully-aromatic polyamide active layers of TFC membranes, the voids fill up with water when immersed in it, and the voids account for a significant volume fraction of the active layers (i.e., 15–32% for the membranes studied). It was concluded that the voids in polyamide active layers do not form passageways connecting the feed and permeate sides, but rather are cavities disconnected from the feed side. In addition, it was also concluded that the globular features observable in TEM images of membrane cross sections that had been previously identified as voids or nodules are indeed voids, and not nodules. The finding that a significant volume fraction of fully-aromatic polyamide active layers corresponds to water-filled voids has deep implications on various aspects of TFC membrane science and technology. For example, we illustrate how the presence of voids can potentially increase the effective water permeability of the active layer by as much as a factor of  $\approx 5$  compared with the case of an equivalent active layer without any voids. The methods developed in this study to measure void volume fraction represent useful tools for future membrane characterization studies, and the void fractions measured can be used as input or calibration parameters in future modeling studies of active layer formation or water and solute transport.

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## 1. Introduction

Thin-film composite (TFC) membranes with polyamide active layers are used in a broad range of applications, including water desalination, hardness removal, and water reuse by nanofiltration (NF) and reverse osmosis (RO), and energy production [1–4]. Polyamide TFC membranes consist of a top ultrathin ( $\sim 20$ – $200$  nm) polyamide active layer, a microporous polysulfone support ( $\sim 20$ – $50$   $\mu\text{m}$ ), and a polyester backing layer ( $\sim 50$ – $150$   $\mu\text{m}$ ) [5–7]. The polyamide active layer constitutes the selective barrier to water and solute permeation [5,8], and thus the physical structure of the active layer likely plays an essential role in the water permeability and solute rejection properties of the membranes [9].

The polyamide active layer of TFC membranes has traditionally been assumed to be a dense polymer phase, with pores, if any, no larger than a few nanometers in diameter. This conceptualization of the active layer is reflected in the two mechanistic models commonly used to describe water and solute permeation through polyamide membranes, the solution-diffusion model [10] and the pore-flow model [11]. The solution-diffusion model assumes that the active layer is dense without any pores [10], and the pore-flow model assumes the existence of nanopores (typically cylindrical with a diameter of a few nanometers or less) that stretch across the active layer within an otherwise dense structure [11,12]. Contrary to this conceptualization of the active layer, recent studies [13–16] suggest that globular features visible in cross-sectional transmission electron microscopy (TEM) images of membrane active layers correspond to voids (i.e., regions without polymer) having tens of nanometers in diameter. It is important to note that the voids suggested in these studies are not the same as

\* Corresponding author. Fax: +1 919 966 7911.  
E-mail address: [coronell@unc.edu](mailto:coronell@unc.edu) (O. Coronell).

the pores in the pore-flow model, as the pores in the pore-flow model connect the feed side and permeate side of membrane active layers and have diameters of a few nanometers while the voids apparently seen in the TEM images do not seem to connect the feed side and permeate side of membrane active layers and have diameters of as much as tens of nanometers.

A different interpretation of the globular features observed in cross-sectional TEM images of polyamide active layers was proposed by Pacheco et al. [17] who indicated that these features correspond to polymer nodules. Based on TEM images of the active layer of a brackish water reverse osmosis (RO) membrane in which globular features 20–60 nm in size were visible, Pacheco et al. further proposed that active layers are composed of a dense nodular base from which the ridge-and-valley structure extends outwards. Similar features to those interpreted as nodules by Pacheco et al. and voids by others [13–16] are visible in TEM images reported elsewhere [18–20], although they were not identified as nodules or voids.

While there is no agreement in the peer-reviewed literature on whether the globular features in TEM images discussed here are voids or dense nodules [21], the features are significantly lighter in shade than the rest of the active layer when bright-field imaging is used [14–20], indicating that they have a lower electron density than the surrounding polymer. Therefore, these features are likely voids, instead of dense nodules, or correspond to regions of significantly lower polymer density. The postulation that the features are voids is supported by the recent scanning electron microscopy (SEM) work by Yan et al. [22] who reported cross-sectional SEM images with features interpreted as voids with sizes of tens to over a hundred of nanometers in diameter. The lack of agreement on whether the globular features are voids or nodules is partially based on the fact that the only evidence supporting either claim are the electron microscopy images themselves which may be affected by the electron beam irradiation during TEM and SEM analysis. If these globular features represent a significant volume fraction of the active layers and are commonly found in fully-aromatic polyamide TFC membranes with a broad range of performance levels, confirming that they are indeed voids would have important implications for the understanding of transport mechanisms of water and contaminants through polyamide membranes since, as described above, current transport models do not account for voids. Confirming the existence of voids and measuring the volume fraction they account for in polyamide active layers would not only provide a more accurate understanding of active layer structure but also enable a more accurate interpretation of active layer characterization data, e.g., partition and diffusion coefficients in polyamide. The confirmation of the existence of voids as common features in the fully-aromatic polyamide active layers of TFC membranes would also indicate to membrane developers that the voids are an active layer property that could potentially be targeted for optimization towards the development of improved membranes.

Accordingly, the objectives of this study were to evaluate whether (1) the globular features observed in the TEM cross-sectional images are in fact voids, (2) voids exist in a broad range of fully-aromatic polyamide TFC membranes, (3) voids account for a significant volume fraction of the active layers, and (4) voids are filled with water when the membranes are immersed in it. An additional objective was to (5) briefly illustrate some of the implications of the existence of water-filled voids on broad aspects of RO/NF membranes science and technology, with an emphasis on the determination of the water transport properties of polyamide active layers. To accomplish these objectives, a broad range of fully-aromatic polyamide TFC membranes were studied, the volume fractions accounted for by the globular features in the active layers were measured by TEM image analyses, and the volume fractions accounted for by voids in the active layers were measured using two non-microscopy techniques – quartz crystal microbalance (QCM)

measurements of water uptake by polyamide active layers and spectroscopic ellipsometry estimates of the refractive indices of active layers. The volume fractions obtained for the globular features through TEM image analyses and voids through QCM and ellipsometry analyses were compared to each other. Similar volume fractions obtained with the different analyses methods would provide evidence in support of the hypothesis that the globular features are actually voids, not nodules, as the methods employed are based on completely different physical principles. Furthermore, elemental mapping of membrane cross sections using energy dispersive X-ray spectroscopy and electron energy loss spectroscopy were also used to evaluate the elemental composition of the globular features so as to ascertain their void or nodular nature. QCM measurements also served to assess whether the voids filled up with water. This study presents experimental results and their corresponding discussion, as well as the implications of the findings to the study and development of polyamide TFC membranes.

## 2. Materials and methods

### 2.1. Target membranes and sample preparation

Five fully-aromatic polyamide TFC membranes of various performance levels were studied: NF90 [23], XLE [24] and SW30HR [25] received as flat sheets in dry state (Dow Filmtec, Minneapolis, MN) and ESPA3 [26] and SWC4+ [27] received as flat sheets in wet state (Hydranautics, Oceanside, CA). ATR-FTIR analyses (see [Section S1 in Supplementary Material](#)) indicated that all membranes have aromatic polyamide active layers and that the active layer of the SW30HR membrane has a coating, which is likely polyvinyl alcohol [28]. Membrane samples were initially prepared as  $2.5 \times 5.0$  cm<sup>2</sup> coupons thoroughly rinsed with and stored in ultrapure water (> 18 M $\Omega$  cm). Before further sample preparation for TEM, QCM, ellipsometry and atomic force microscopy (AFM) analyses, the coupons were blot-dried by placing them between two filter paper circles (qualitative grade circles No.1, 9 cm in diameter, Whatman) and applying fingertip pressure [29,30]. Pressure exerted in this manner is orders of magnitude lower than the pressure that RO/NF membranes experience during membrane operation in treatment plants (~100–1200 psi). The coupons were then air dried overnight.

### 2.2. TEM analyses

For TEM analyses, a membrane sample preparation procedure similar to that described by Tang et al. [18] was used. In brief, membrane samples were dehydrated with 100% ethanol, infiltrated and embedded with LR White resin (London Resin Co., Reading, UK) diluted in ethanol, cured at 48 °C for 3 days, and cut into thin (~90–100 nm) slices with a Sorvall MT 6000 Ultramicrotome (RMC Co., Tucson, AR). TEM imaging of membrane cross-sections was performed with a JEOL 100CX II TEM (JEOL USA, Peabody, MA) at an acceleration voltage of 80 kV. Three images were taken for each membrane studied at magnifications of 29,000 $\times$  or 72,000 $\times$  depending on the thickness of the active layers. Control TEM images were obtained for SWC4+ membrane samples dried using supercritical CO<sub>2</sub> drying, which confirmed that air/ethanol drying did not affect the active layer structure (see [Section S2 in Supplementary Material](#)).

### 2.3. Scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) and electron energy loss spectroscopy (STEM-EELS) analyses

Membrane sample preparation and sectioning for STEM-EDS and STEM-EELS analyses were performed in the same manner as

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