Obtaining accurate cross-section images of supported polymeric and inorganic membrane structures

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Graphical Abstract

Keywords

Focused Ion Beam cross-section; multilayer electron imaging; polymer membrane; hybrid membrane; microstructure.

Abstract

Detailed and accurate information about the morphology of supported membranes structures is important for the analysis of their performance and fabrication. In this work it is shown that Focused Ion Beam (FIB) nano-machining can be used to provide such information for polymeric and inorganic membrane layers and composite structures containing those layers. Single-sided cuts are used for scanning electron microscopy (SEM) observations; ~100 nm thin slabs obtained with two-sided cuts are used for transmission electron microscopy (TEM) imaging. Details of the FIB milling are provided in addition to examples of cross-sections of polymer, hybrid and inorganic structures. It is shown that the quality of cross-section information, obtained with FIB, is superior to that obtained with transmission electron microscopy of micro-tome sections. In addition it is shown how Energy Dispersive X-ray Spectroscopy (EDS) mapping of FIB cross-sections provides information about the relation between chemical composition and membrane structure that cannot be obtained otherwise.

1. Introduction

Polymer membranes [1] and ceramic membranes [2] have a complex morphology [3]; their overall supported membrane structure is often multi-layered and/or graded. In such a structure one distinguishes, going from feed to permeate side:

- A (thin) membrane cover layer for protection and/or defect abatement [4].
- The actual separative membrane layer, often as thin as possible (given constraints of fabrication and defect control).
- One or more intermediate layers that form a bridge between a supporting layer with larger pores and layers with smaller pores or a dense structure.
- A support or carrier layer that provides strength to the overall membrane structure.

Since the support or carrier layer is load-bearing, it is generally much thicker than the other layers. Its pore structure is then preferably designed such that its flow resistance is small compared to that of the membrane [5]. Polymer membrane structures made by phase-inversion do have a graded structure but they cannot be fully described as a discrete multi-layer structure. However, for the sake of simplicity, we follow the above terminology to describe a typical layer structure in terms of cover-on-membrane-on-intermediate-on-support-on-carrier. Where we refer to polymer(s) we mean organic-monomer-based polymer(s). Solid phase particle and grain sizes are referred to as $\emptyset_s$ while pore sizes are indicated with $\emptyset_p$.

Figure 1: TEM image of a cross section slab of a 100 nm thick scandium-stabilized zirconia (SSZ) membrane on porous alumina. The cross-section was made by Focused Ion Beam milling. In this structure membrane penetration in the support is fully avoided by pretreatment of the support with polyvinylpyrrolidone, followed by burnout after membrane deposition.

Individual layers in the membrane multi-layer structure generally have a microstructure containing one or more solid phases, and possibly a pore phase. The layer microstructure is characterized by the size, shape, spatial distribution and connectivity of the individual solid and phases. Near layer boundaries, the structure often deviates from that of the bulk layer due to interpenetration of layer components. Obvious deviations from the quasi-homogeneous [3] layer structure are considered as defects. In any case the occurrence of defects adversely affects membrane fabrication and performance. Pin-hole defects can be described as large open pores that connect the two layer boundaries. They can have a deleterious effect on membrane selectivity and the integrity of subsequent layers.

Detailed insights into the actual membrane structure are important for the design and fabrication of membranes, as well as for the understanding of overall membrane transport properties, structural degradation and fouling. For very thin, flat membranes, as shown in figure 1, a substantial spreading resistance occurs, since transport in the feed/permeate direction is partly blocked by the underlying support. Interlayer penetration (as shown in figure 2), over a length X_i , results in a

significant increase in transport resistance, much larger than the resistance of a top layer with thickness X_i . Due to the combined effect of tortuosity τ and porosity ϕ_p , the resistance increases by a total factor of $\tau \times 1/\phi_p$: the average path length increases by τ and the space available for gas transport is divided by ϕ_p . In randomly packed structures, with typical values $\phi_p \sim 0.3$ and $\tau \sim 3$, the resulting increase becomes $\sim 10\times$. Consequently, accurate characterization of membrane layer inter-penetration can be important in microstructural optimization. Additionally, since gas transport in membranes is often seriously affected by defects, knowledge of the morphology and location of defects is important to establish their origin and effect.

Figure 2: Three-layer structure SEM single sided cut. Substantial interlayer penetration occurred between the layer with 300 nm α - Al_2O_3 particles, and the layer with $3 \mu\text{m}$ α - Al_2O_3 particles.

Characterization methods that offer microstructural insights are divided into non-destructive and destructive. The *non-destructive* methods include measurement of the transport properties proper, permeation porometry [6] and layer thickness measurements by spectroscopic ellipsometry [7]. These methods can provide characteristics for the average layer. Ellipsometry can be applied with flat and slightly curved surfaces; it requires a smooth support surface and transparent membranes. State-of-the-art polymer membranes are sufficiently smooth to obtain an accurate membrane thickness by ellipsometry. Ellipsometry of inorganic membranes requires smooth supporting surfaces. Optical microscopy can be used to inspect larger surface defects. The *destructive* methods include scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of surfaces and cross-sections. These

methods typically require the application of conducting layers to avoid surface charging, and exposure of the membrane cross-section. The conducting layers can obscure details, while

Figure 3: γ -alumina on α - Al_2O_3 (a): fracture; (b): polished; (c): FIB.

exposure of the membrane has to be done so that a representative image can be taken. Exposure methods include fracturing of brittle membrane structures, focused ion beam (FIB) milling [8]-[9], diamond knife cutting and microtoming [10]. Polymer structures may be brought into a brittle condition by freezing in liquid N₂ [11] and more detail may be preserved by prior impregnation with a resin [12] or simple liquid such as iso-propanol. Nevertheless, in the creation of cross-sections by fracture of knife-cutting, local deformation may occur due to fracture propagation. The fracture may follow a preferential path [13] and fracture debris may become incorporated in the visible microstructure, see figure 3 (a). Moreover, the solid fracture surfaces vary in depth so that their imaging contains a mixture of 2D and 3D information that is difficult to deconvolute. All these effects result in a non-representative image, regardless of the imaging method. Better information would be obtained in both 2D and 3D from clean 2D cuts through the solid phase. The major obstacle for obtaining good TEM images is in obtaining microtome sections that are sufficiently thin and uniform to reveal the morphology. Polishing of polymer structures is virtually impossible; polishing of ceramic structures leads to effects similar to fracture and, for porous structures, also very serious impregnation with debris which obliterates almost all detail, see figure 3 (b).

Focused ion beams using field emission ion sources were first developed in 1970s [14].

The use of FIB systems for TEM sample preparation was introduced and gradually expanded in the 1990's [8]-[9]. Dual focused ion beam/electron beam systems with high resolution <1 nm were developed in the past decade, and can provide a true 2D cross-section of a membrane microstructure while the depth of structural damage can be limited to ~ 1 nm by deposition of a Pt bar on the top

surface. The cross-sections can be made by shearing of fracture surface or by digging a trench, see figure 4. To prepare electron-transparent samples, three trenches can be dug: one at either side and one at the bottom of a thin slab of sample. This slab is then completely cut off from the trenches and lifted on a TEM grid. In the membrane literature, FIB is fairly well-established for fully ceramic structures [15] see figure 3 (c) [16] but not for polymer and inorganic-polymer hybrid structures. Particular complications for polymer-containing structures are (i) higher sensitivity to beam damage due to softness of the material, (ii) deformation due to surface charging, and (iii) large differences between organic and inorganic phases, which may obscure the details within each phase.

Polymer and hybrid polymer-inorganic structures for non-membrane applications have been previously studied by FIB. If the polymer layers [17][18] are dense and homogeneous, the acquired information includes thickness and possibly inter-layer roughness. Examples of non-

Figure 4: Trench and snap off TEM sample; the transmission image is shown in figure 3 (c).

homogenous materials examined by FIB include photographic film with dispersed color-absorbing grains [19] and aluminum particles dispersed in polyethylene [20]. Microstructures of biological samples and cells, with a length scale and heterogeneity similar to that of a membrane, were imaged using a cryo-transfer system fitted into a modified FIB/SEM setup [21]. More recently, studies of FIB damage have been reported on soft materials, including lignite coal and polyacrylamide, PAAm [22], or amorphous polycarbonate, PC [23]. It was found that chemical bond alteration is possible, and that low-levels (0.1% wt or less) of Ga^+ implantation may affect sample stiffness.

3D structure mappings are obtained by application of multiple cycles of FIB, each time followed by imaging of the exposed surface. This technique has been used to study, among others, polymer materials [24] and biological samples [25].

Whereas cryo-imaging may improve the image quality and 3D mapping methods can provide additional insight, they require hardware/software adaptations and/or considerably higher working time. It is the purpose of this paper to focus on membrane structures that are composed partly or exclusively of polymer layers. For these structures, it is shown that with careful application of the basic FIB technique, accurate and representative 2D cross-section images of good quality with meaningful microstructural information were obtained.

2. Experimental

2.1 Materials selection and membrane preparation

Polysulfone (PSF) membranes with a nominal pore diameter of 50 nm were purchased from NL Chemical Technology, Inc.; PBMK, Biomax polyethersulfone (PES) 1000 kDa MWCO ultrafiltration discs were purchased from EMD Millipore. Boehmite (approximately AlOOH)

membranes on PES supports were prepared used the protocol described in [16], followed by drying at 110°C for 1 h. These samples are referred to as Boehmite;PES in the remainder of the text. On other PES supports, a layer of α -Al₂O₃ particles with $\varnothing_s \sim 300$ nm (AKP30 powder, Sumitomo Chemical) was deposited by slip casting. A cover layer of polydimethylsiloxane, PDMS (Wacker Chemie), was subsequently deposited by spin-coating, followed by curing at 100°C for 1 h. This sample is referred to as PDMS; α -Al₂O₃;PES. The hybrid structures are currently investigated for cost-effective gas separation applications [2].

2.2 Characterization

FIB samples were prepared with Helios NanoLab600 DualBeam equipment (FEI), which included an Energy Dispersive X-ray (EDS) unit (INCAPentaFETx3, Oxford Instruments). Prior to the actual milling procedure, they were provided with a 40 nm Au layer by sputtering to improve conductivity. In addition a 20×1×0.6 μ m Pt bar was deposited on top of the area to be milled by using ion beam assisted chemical vapor deposition. A voltage of 30 kV was applied to the Pt deposition needle resulting in a 0.28 nA current. Cross-sections for SEM examination were trenced with a 2.8 nA Ga ion beam using cleaning cross section milling at 30 kV. Higher currents result in high roughness in the cross sections due to the large spot size. Afterwards, a polishing current of 0.96 nA was applied to minimize roughness. SEM images were obtained using secondary electrons at a voltage of 5 kV, 10 kV or 20 kV with a current of 0.69 nA or 0.43 nA. The voltage-current combination was optimized for every sample to provide the highest quality images. A typical value for the electron beam dwell time was 20 μ s. No obvious beam damage was observed under our experimental conditions. EDS was performed on an FIB cut of the sample PDMS; α -Al₂O₃;PES with a beam energy of 10 keV, and an acquisition time of 30 min.

Specimens for TEM observation underwent the same trenching process for both sides and were thinned gradually with a smaller beam current of 0.28 nA to obtain a sample thickness of <300 nm. The sample was attached to an OmniProbe AutoProbe™ 200 in-situ sample lift-out system, by small area Pt deposition on the previously deposited Pt bar, and mounted on a post of a FIB/TEM grid (Ted Pella Inc.) by Pt welding. Transmission electron microscopy (TEM) was performed at a 120 kV Philips CM12. For comparison, a PSF sample was embedded in epoxy resin (Eponate 12), cured and sectioned on a Leica EM UC6 ultra microtome before TEM imaging.

3. Results and Discussion

Cross sections of PSF by FIB nanomachining and microtoming are shown in figure 5. Both cross-sections reveal a porous morphology.

The FIB sample (figure 5 (a)) shows a clear cross-sectional cut with a uniform pore distribution at any constant depth, and a gradual decrease of pore size towards the top layer, as expected. The very small pores in the top skin layer (estimated as ~ 10 nm from surface SEM micrographs, not presented here) are also visible. On the other hand, the microtomed sample (figure 5 (b)) reveals a more irregular pore morphology without the expected grading of pore size, and with the top layer appearing as dense. The observed cross-sectional pore sizes are also different for the two samples. 2D pore sizes were estimated by taking a line parallel to the surface at a depth of $2\ \mu\text{m}$ and measuring the lengths of the line between their intercepts with pore boundaries.

3D average values were then obtained by

Figure 5: PSF cross-section images. (a): SEM of an FIB cut. (b): TEM of a 100 nm thick microtome slab. (c): TEM of a 200 nm FIB slab.

multiplying the 2D values by $4/\pi$ [26]. This resulted in $\varnothing_p = 46$ nm for the FIB/SEM cross-section, in good agreement with the nominal value of 50 nm. On the other hand $\varnothing_p = 103$ nm was obtained for the microtome cross-section at the same depth. All this indicates that FIB milling may result in less distortion of porous polymer features, compared to microtome cutting.

A Boehmite;PES structure is shown in figure 6.

It was found that a ~180 nm thick layer of Boehmite particles was present on the PES support. The Boehmite particles were reported to have a diameter of ~20 nm and a thickness of ~3 nm [16]. The cross sectional images (figure 5 (a)) revealed no visible cracks, good adhesion (no delamination), and no interpenetration. In addition, with the FIB/SEM equipment that was used, it was possible to simultaneously observe the top surface (figure 5 (b)) and the cross section.

Figure 6: Boehmite;PES membrane: (a) cross-sectional view, made by FIB; (b) plan-view showing boundaries between 300 nm Boehmite islands, likely due to drying shrinkage.

Figure 7: (a) FIB cross-section of a PDMS; α -Al₂O₃;PES membrane observed by SEM; (b) simplified proposed membrane structure and its orientation; (c-g) EDS mapping for Al, O, S, Si and Pt. All EDS images have the same contrast levels and correspond to the area imaged in (a). Solid and dashed lines were added for alignment purposes. Pseudo-colors are used to enhance visibility. (h) Lower magnification image that includes part of the sample surface.

Finally, FIB can be combined with EDS to provide additional information. An example for PDMS; α -Al₂O₃;PES membrane, is shown in figure 7(a,h). In this figure the α -Al₂O₃ particles ($\varnothing_s = 300$ nm) were clearly visible, as are the pores of the support. Figure 7(c-g) shows the results of EDS mapping for the elements Pt, Al, O, S, Si. Al is indicative for the presence of Al₂O₃, S for PES, and Si for PDMS. O is present in all these compounds, but with the highest ratio in Al₂O₃. No Ga was detected while it was detectable in previous samples where an ion beam current of >2.8 nA was used.

Both the SEM image (figure 7(a)) and the EDS mappings correspond to the projection of the cross section perpendicular to the beam direction (figure 7(b)). The secondary electrons used for the SEM image originate from the surface only. On the other hand, since the EDS sampling depth is on the order of a μ m, the EDS mapping also includes information from part of the material volume. Due to the stage tilt angle (52°) the mapping also contains information about underlying layers. Taking this into account, there is good agreement between the EDS data (figures 7(c-g)), the SEM image (figure 7(a)) and the proposed microstructure (figure 7(b)). The apparently higher concentration of S in the upper part is attributed to the higher density of the upper PES region (including the skin layer). However, the possibility of penetration of the Al₂O₃ particles in the PES support could not be excluded.

The FIB technique was also found to be applicable for other inorganic-on-polymer layers, including zeolite Y and ceria on PES supports. In all cases, acquiring a satisfactory image required more effort than what was needed for cross-sections of fully inorganic structures. The overall duration of milling and imaging had to be kept low, to avoid adverse effects by surface charging and beam damage due to softness of material. In addition, it was important to keep the milling time short to minimize the distortion of both organic and inorganic phases. The presence

of a “thick” Pt bar deposited on the top surface was essential to provide sufficient rigidity during the milling process.

4. Conclusion

Characterization of membrane multi-layer structures can be divided into non-destructive and destructive. Among the non-destructive methods spectroscopic ellipsometry, optical microscopy and interpretation of transport properties are the most suitable. Possible destructive methods include SEM and TEM of fracture surfaces, microtome cuts, and FIB cross-sections. Inspection of fracture surfaces gives some qualitative information about membrane layer thickness. FIB nanomachining can be used to expose representative cross-sections of porous polymer, inorganic/polymer hybrid and inorganic membrane structures. FIB cross-sections for polymer-based structures require special precautions for mechanical stabilization of the membrane. However, the cross section quality is higher in comparison to microtome cross-sections, and more representative of the layer micro-structure. Information obtained from SEM and TEM of FIB cross-sections, possibly combined by EDS mapping, includes layer thickness, layer inhomogeneity such as defects, pore morphology and size grading, layer composition, infusion with chemicals, and interpenetration between layers. To the author's knowledge the detailed and fully representative structures for polymeric and hybrid membrane structures in this paper are the first ever reported.

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Figure Captions

Graphical Abstract: (No caption.)

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Figure 3: γ -alumina on AKP30 α -Al₂O₃ (a): fracture; (b): polished; (c): FIB.

Figure 4: Trench and snap off TEM sample; the transmission image is shown in figure 2 (c).

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