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X-ray tomography-assisted study of a phase inversion process in ceramic hollow fiber systems – Towards practical structural design

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ABSTRACT

Phase inversion-assisted extrusion processes provide a feasible approach for the development of micro-structured ceramic hollow fibers. The mass transport of the hollow fiber, which is closely correlated to the pore structure, is especially important in the application of fuel cell electrodes and membrane reactors. Whilst the relationship between the pore microstructure and the fabrication factors has been the subject of significant investigations, there remains much disagreement in the literature. Recent development in X-ray computed tomography (CT) has enabled new insight into 3D microstructures, which could help to realize practical morphology design and optimization. In this study, a series of alumina hollow fibers have been prepared with varied polymer binder (polyethersulfone, PESf) concentration and new polymer-based internal coagulant (aqueous solution of polyvinyl alcohol, PVA). For the first time, the micro-channels were characterized in 3D using X-ray CT to determine micro-channel densities and diameters in the radial direction, as well as the 2D measurement of the pore size in the sponge-like layer. Water permeation tests were then conducted to correlate the micro-structure of the hollow fiber to the permeability. Results show that the diameter of the micro-channels decreases as the concentration of polymer binder increases, but the pore size in the spongy-like layer becomes larger. When the polymer binder concentration is increased from 16 wt% to 30 wt%, the maximum micro-channel diameter is almost halved (from 29 to 15 μm), and the radial length is 60% longer, whereas the mean flow pore size in the sponge-like layer is increased from approximately 288 to 422 nm. Larger pore size in the spongy-like layer of the high PVA concentration sample contributes to a better permeability (pure water flux almost doubled), but the dimension of the micro-channels is less important. This study provides a new approach to optimize fabrication of hollow fibers for various applications.

1. Introduction

Ceramic membranes have generated a considerable amount of research interest in recent decades for diverse applications such as filtration, desalination, gas separation and membrane reactors and as electrodes for tubular solid oxide fuel cells (SOFC) [1]. Compared to polymeric membranes, ceramic membrane systems display many benefits, including excellent thermal and chemical stability, enabling operation at high temperature and pressure, and under corrosive environments. Moreover, improved mechanical robustness enables easy cleaning of membrane modules and subsequently enhanced long-term operation. Among various designs of ceramic membranes, the hollow fiber geometry shows a unique feature of superior surface area to volume ratio, which is typically more than one order of magnitude higher than planar and monolithic designs [1].

In terms of fabrication techniques, phase inversion-assisted extrusion has drawn an increasing level of attention recently [1–5]. Compared to other fabrication routes, the phase inversion process leads to a unique, asymmetric structure of resultant hollow fiber membranes, which allows them to be not only directly used in many separation processes, but also to serve as a porous support for composite membrane preparation. However, this technique is yet to be applied in large-scale applications due to the deterrent of system complexity: generally, the process includes the immersion of a slurry, (which is mainly composed of ceramic powder, solvent and polymer binder), into a non-solvent bath; such dynamic manufacturing processes involve continuous solvent/non-solvent exchange and polymer binder precipitation. The final morphology depends significantly on a

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number of factors, such as suspension composition, selection of coagulant and corresponding extrusion rates. The sensitivity of the hollow fiber microstructure to different parameters can lead to poor repeatability between batches. The internal coagulant is critical in determining the lumen shape and membrane morphology, particularly during dry-jet, wet spinning processes. Despite being almost exclusively applied as an internal coagulant, water is more likely to lead to the formation of abnormal structures due to its negligible viscosity, resulting in irregular cross-section shape [6–8], eccentric lumen [9,10] and non-uniform structure throughout the fiber.

The polymer binder is another critical component affecting the hollow fiber properties and its effects have been investigated in previous work [5,7,11]. It has been widely acknowledged that the microstructure of the resultant membrane (porosity, pore size distribution, tortuosity, etc.) and subsequently the mass transport properties (gas/liquid permeability) are strongly dependent on polymer binder selection and concentration in the suspension. In spite of this, the micro-channels have received limited attention, mainly due to the lack of approach providing detailed insight into the actual interaction between the polymer binder and the microstructure of the porous micro-channel region.

Conventionally, microstructural analysis is predominantly based on 2D imaging techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). However, these 2-D techniques do not give access to the actual 3D shape and spatial distribution of the microstructure and require significant repetition to obtain statistically relevant results. Recently, focused ion-beam SEM (FIB-SEM) has received significant research attention [12–18] as it enables experimentalists to understand the variation of microstructure in 3D, beneath the sample surface. However, the long data acquisition time restricts the sample volume investigated and moreover, this destructive method makes it impossible for repeated, or time-lapse testing. X-ray computed tomography (CT) is a popular non-destructive technique widely used for 3D visualisation and characterization of materials by back-projecting sequential 2-D projections to form a virtual 3D volume. This technique has been applied to the study of hollow fiber membranes to relate the morphologies of the pores to processing conditions, to explore the mechanisms of the macro-void initiation, and evaluate the effect of solution saturation [13,14,19].

In this paper we develop this methodology and present new geometrical metrics for characterization of micro-channel structures, aiming for (1) understanding the effects of polymer binder concentration on the microstructure of the micro-channels and the “sponge” region in alumina hollow fiber membranes fabricated by a new polymer-based internal coagulant (aqueous solution of polyvinyl alcohol, PVA); (2) correlating the variations of the permeability to the microstructure and assessing the dominating factors affecting mass transport properties.

For the first time, X-ray CT is used to quantify the micro-channel densities and the cross-sectional dimension of the micro-channels along the radial direction. This study can significantly contribute to the knowledge of processing factors determining the macroscopic and microscopic properties of hollow fiber membrane for various applications.

2. Experimental

2.1. Materials

Aluminium oxide powders of 0.35 μm (alpha, 99.85% metals basis, specific surface area 4.5 $m^2 g^{-1}$) were purchased from Advanced Materials (USA) and used as supplied. Polyethersulfone (PESf, Radal A300, Ameco Performance, USA), Arlacel P135 (polyethyleneglycol 30-dipolyhydroxystearate, Uniqema) and polyvinyl alcohol (PVA, Approx. M.W. 145000, Merck Schuchardt, Germany) were applied as binder, dispersant and internal coagulant, respectively. N-Methyl-2-pyyrolidone (HPLC grade, VWR International) was used as the solvent.

Table 1
Suspension compositions and fabricating conditions of different alumina hollow fibers.

	Solid loading (%)	Polymer concentration (polymer/solvent)	PVA solution extrusion rates (ml min^{-1})	Suspension extrusion rate (ml min^{-1})	Air gap (cm)
A1	58.1	16 wt%	10	8	2
A2			15		
B1		20 wt%	10		
B2			15		
C1		25 wt%	10		
C2			15		
D1		30 wt%	10		
D2			15		

2.2. Fabrication of alumina hollow fibers

Aluminium oxide powders were first mixed with the solvent and dispersant and milled for 48 h in a planetary ball mill at 260 rpm (SFM-1, MTI Corporation). The milling was further conducted for 48 h after adding in polymer binder to obtain homogeneous suspensions. The suspension was degassed under vacuum to eliminate air bubbles trapped inside before being transferred into stainless steel syringes. Both suspension and PVA aqueous solution (internal coagulant) were extruded through a tube-in-orifice spinneret into an external coagulant bath to form the hollow fiber precursors, during which the extrusion rates of both components were precisely controlled by syringe pumps (Harvard PHD22/200HPsi). Details of the compositions and fabrication conditions can be found in Table 1. Hollow fiber samples are classified into four groups, denoted from A to D, with corresponding polymer loading ranging from 16 to 30 wt%. Within each group, two different extrusion rates of internal coagulant have been attempted, which are 10 and 15 ml min^{-1}. The precursors were left in the coagulation bath overnight before being straightened and dried. Then, the precursors underwent a sintering process (Carbolite furnace) to form the final ceramic hollow fibers: the temperature was increased to 600 °C at a heating rate of 2 °C min^{-1} and held for 2 h, and then heated to the target temperature of 1500 °C at a rate of 5 °C min^{-1} and held for 4 h, finally the furnace was cooled to room temperature at a rate of 5 °C min^{-1}.

2.3. Materials characterization

Prepared materials were characterized using SEM (JEOL JSM-5610 LV). A clean cross section was obtained by snapping the fibers and samples were subsequently placed vertically on a metal holder. Prior to the imaging, samples were sputter coated with gold (EMITECH Model K550). Secondary electron (SE) imaging mode was adopted to obtain images at varying magnifications using an acceleration voltage of 20 kV. The pore size in sponge-like layer is determined by gas–liquid displacement measurements using PoroLux 100 Porometer with commercial wetting liquid (Porefil, surface tension of 16 mN m^{-1}). Three specimens were tested for each type of sample, with standard deviations of pore size less than 5%. Pure water flux was measured using a custom-designed dead-end system: three samples were tested for each type of membrane with an in-out mode and the average value was calculated with standard deviations of less than 10%. Due to the differences in morphology between different samples, the outer diameter of fiber was used to calculate the surface area.

Non-destructive X-ray computed tomography (CT) was performed using a Zeiss Xradia Versa 520 X-ray microscope operated at 80 kV [20]. The source to test-piece distance and test-piece to detector distance are 13 and 30 mm, respectively, a 4X optically coupled objective lens was applied to achieve a resolution of 1.03 μm and a cylindrical imaged volume of 2×2×2 mm^3. During sample rotation, 2001 projections were collected with 18 s exposure time using a 16-bit