Journal of Membrane Science 503 (2016) 48–58

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

New designs of ceramic hollow fibres toward broadened applications

Melanie Lee, Bo Wang, K. Li *

Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK

ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form
8 December 2015
Accepted 23 December 2015
Available online 28 December 2015

Keywords:
Asymmetric ceramic membranes
Hollow fibre membranes
Micro-channels

ABSTRACT

Three structural designs for ceramic membranes have been achieved for the first time through the co-extrusion of polymeric and ceramic layers. During co-extrusion, micro-channels are initiated due to the Rayleigh–Taylor instability and they propagate through the different layers. The polymeric layer(s) is then calcined off during the heat treatment step, which opens the micro-channels and following sintering a ceramic membrane with open micro-channels ranging from a few to a few tens of micrometres in diameter can be formed. These long, straight and non-tortuous micro-channels can be controlled to be open at any or all of the surfaces. Design 1 has open micro-channels passing through the entire membrane wall, Design 2 has a separation layer at the lumen and open micro-channels at the shell side, and Design 3 has open micro-channels from both lumen and shell sides sandwiching a separation layer of sponge-like structure. Aside from having much improved mass transfer property due to the reduced effective membrane thickness, they can be easily incorporated into hybrid systems with anticipated improvements in unit compactness and performance. The pure water permeation of Design 2 reached up to 159,000 L/m^2 h bar with pore sizes in the micro-filtration range. The micro-channels are easily accessible from the shell/lumen side; therefore catalysts or adsorbents can be easily deposited into the micro-channels. Examples of possible applications include a high-efficiency dispersing device realised with Design 1; a gas chromatography column for gas separation with very low pressure drop realised with Design 2 and a highly compact membrane micro-reactor for consecutive reactions proposed with Design 3.

1. Introduction

The combined phase inversion and sintering method is a promising method for creating ceramic membranes that have shown various advantages over traditional methods. Firstly, they can produce asymmetric membranes in a single step requiring one heat treatment session only, and secondly, the method is versatile and can be used to form a wide range of different membrane configurations: flat discs, hollow fibres, multi-channel monoliths, etc [1–4]. The ability to form finger-like micro-channels in the membranes due to interfacial instabilities not only reduces mass transfer resistance, giving rise to competitive pure water permeation fluxes, but also widens the possible applications of these ceramic membranes [4–11].

The majority of the ceramic membranes fabricated by this method in literature consist of dense inner and outer surfaces and regions of micro-channels, which may sometimes sandwich a layer of sponge-like structure. The surface with the smallest packing pore size would act as the separation layer. Hence, if the pore size of the separation surface meets separation requirements, the other surface or sponge-like layers do not offer any improvements in selectivity, but instead creates additional resistances to mass transfer. By eliminating the redundant dense surface and sponge-like layer, the pure water flux of the membranes can be dramatically increased [2]. Furthermore, the micro-channels are desirable crevices where catalysts or other active components can be deposited or coated to form hybrid systems [1,12], but the existence of the dense surfaces prohibit access to these micro-channels unless solution techniques are employed.

For flat disc membranes, it is very simple to mechanically open the micro-channels via sanding off the dense surface and/or the sponge-like layer. However, this is much more difficult to do in hollow fibre membranes. So far, research has been carried out to obtain openings on hollow fibre inner surfaces, and open micro-channels at the lumen side have been achieved in several studies by incorporating a solvent into the bore fluid [3,13,14]. This configuration has been shown to reduce the mass transfer resistance and thus substantially improve permeation fluxes. However, there may be applications whereby other configurations are desired, for example, open micro-channels at the outer surface only, or open channels throughout the entire membrane cross-section. The flexibility of the combined phase inversion and sintering method means that the cross-sectional structure of hollow fibres can be

* Corresponding author.
E-mail address: kang.li@imperial.ac.uk (K. Li).

http://dx.doi.org/10.1016/j.memsci.2015.12.047
0376-7388/

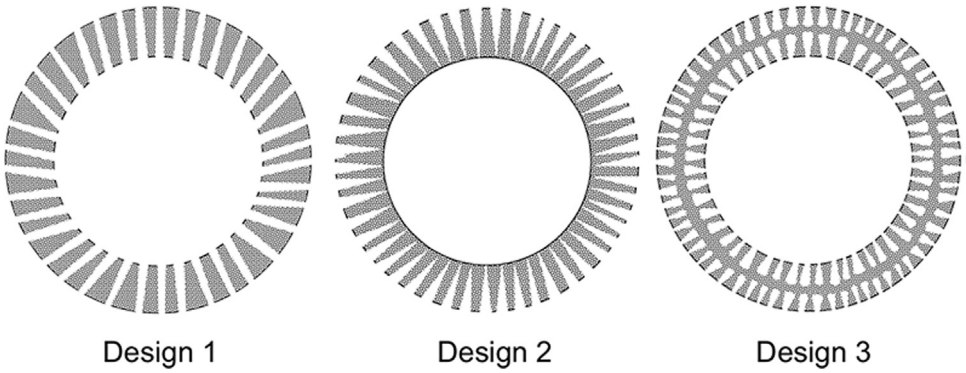

Fig. 1. Schematic of the three types of hollow fibre cross-section structural designs achievable through co-extrusion of ceramic and polymeric layers.

Table 1
Composition of the 3 designs' precursor layers.

Layer	Composition (%)							
	Design 1		Design 2		Design 3		Common single layer hollow fibre	
Ceramic layer	NMP	33.6	DMSO	33.6	NMP	33.6	DMSO	33.6
	Alumina	60.0	Alumina	60.0	Alumina	60.0	Alumina	60.0
	PESf	6.0	PESf	6.0	PESf	6.0	PESf	6.0
	A135	0.4	A135	0.4	A135	0.4	A135	0.4
Polymeric layer	NMP	80.0	TEP	80.0	NMP	80.0	N.A.	
	PESf	20.0	PESf	20.0	PESf	20.0		
Bore fluid	NMP	70.0	Water	100.0	Water	100.0	Water	100.0
	Ethanol	30.0						

designed and tailored as desired. In this study, three significantly different membrane cross-sectional structures with open micro-channels have been designed and fabricated via the co-extrusion of polymeric and ceramic layers. The co-extrusion of multiple layers has been used extensively in both polymeric and ceramic membranes, broadening their applications whilst reducing fabrication costs [15–18]. Different materials can be used in the different layers to increase the functionality of the membranes. Dual-layered polymeric membranes have found use in applications such as pervaporation and membrane distillation and triple-layered membranes in solid oxide fuel cells [19,20]. However, the multi-layered membranes in literature are mostly entirely organic, or inorganic, and the finger-like structures in these membranes are still enclosed inside the membranes. In this study, polymeric and ceramic layers were co-extruded, and following heat treatment the polymeric layer(s) are removed, leaving unique single-layered ceramic membrane structures. For the first time, ceramic hollow fibres with open micro-channels at the desired surface(s) have been formed in a single spinning step as shown in Fig. 1 and their properties such as cross-sectional morphology, pore size distribution, mechanical stability and pure water flux were systematically investigated and their potential applications were discussed.

2. Experiments

2.1. Materials

Aluminium oxide (Al_2O_3) (alpha, 99.9% metals basis, surface area 6–8 m^2/g, mean particle size (d50) 1 μm, Inframat Corporation) was used as supplied. Polyethersulfone (PESf) (Radal A300, Ameco Performance, USA) was used as the polymeric binder. Dimethyl sulphoxide (DMSO, HPLC grade, VWR), N-methyl-2-pyrrolidone (NMP, HPLC grade, VWR), Triethyl phosphate (TEP, HPLC grade, Sigma Aldrich) were used as the solvents. Arlacel P135 (polyethylene glycol 30-dipolyhydroxystearate, Uniqema) is used as the additive. De-ionised water and ethanol (HPLC grade, VWR) were used as the coagulants.

2.2. Fabrication of micro-structured alumina hollow fibre membranes

The fabrication process is based on the phase-inversion technique used to prepare multi-layer hollow fibres, whereby a ceramic suspension layer served as the precursor, and polymeric layers were used as sacrificial layer to generate the desired structures. A uniform suspension composed of ceramic particles, solvent and polymeric binder, as well as an additive acting as a dispersant, was prepared via ball milling, and its composition is listed in Table 1. The polymer dopes were prepared by mechanically stirring PESf in NMP under room temperature for 24 h for Designs 1 and 3, and PESf in TEP under 80 °C for 48 h for Design 2. The ceramic suspension was then degassed under vacuum with stirring to fully remove bubbles, and then transferred into a 200 mL stainless steel syringe that was controlled by a syringe pump (Harvard PHD22/200 HPsi and KDS410). The polymer dopes were left in an oven overnight at 80 °C to degas and then transferred into a 100 mL stainless steel syringe controlled by another syringe pump. The ceramic suspension and polymer dopes were thus be extruded through the spinnerets shown in Fig. 2, into the external coagulation bath. Meanwhile, DI water or a solvent and non-solvent mixture is introduced through the spinnerets via another syringe pump. The precursor hollow fibre membranes were removed from the external coagulant bath when phase-inversion was complete, and were dried and straightened at room temperature. They were then cut into the required length for subsequent calcination and sintering. Further details on the parameters of the fabrication process are listed in Tables 1 and 2. For comparison, a conventional single-layer hollow fibre was also prepared, and the fabrication parameters are also included in Tables 1 and 2.