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A controlled sintering process for more permeable ceramic hollow fibre membranes

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ABSTRACT

In this study, a new controlled sintering process has been proposed to improve the water permeation of asymmetric alumina hollow fibre membranes. In this process, polymer binder (PESf) in precursor fibres is purposely pre-treated in static air at selected temperatures (400–600 °C) to have it partially removed, prior to be converted into carbon in a second sintering step (1450 °C) under an oxygen free environment. During the second sintering step, proper bounding between ceramic particles takes place, while the growth of ceramic grains is effectively suppressed due to the presence of carbon. The carbon in the voids formed by particle packing also acts as a pore structure "stabilizer" and can be removed easily via subsequent thermal treatment in static air at 800 °C. Compared to the membranes with the same asymmetric structure and sintered in static air only (i.e. normal sintering), the membranes sintered using the new controlled sintering process shows water permeation flux is approximately 13 times higher, together with comparable mechanical strength. Moreover, this original concept of using the polymer binder to design the pore structure of ceramic membranes can be transferred to other inorganic materials.

1. Introduction

A phase inversion assisted process involving viscous fingering phenomenon and sintering has been recently well investigated in fabricating inorganic hollow fibre membranes for various applications [1–6]. In contrast to other processes in fabricating ceramic micro-tubes of similar sizes, the unique difference lies in its flexibility in forming radial micro-channels, leading to a number of new asymmetric membrane structures that can hardly be achieved in a single-step via conventional fabrication techniques.

In such a membrane fabrication process, generally a uniform mixture/suspension of ceramic particles, solvent, polymer binder and additives is extruded through a tube-in-orifice spinneret, before entering an external coagulation bath (with or without an air gap). Meanwhile, another stream of solvent or non-solvent flows through the central bore of the spinneret, forming the hollow fibre configuration. The morphology of hollow fibres can be controlled by adjusting a number of process parameters such as suspension composition, air gap, extrusion rate and bore liquid flow rate etc. PESf is one of the most widely used polymeric binders in this process. Its function was first considered as a binder connecting ceramic particles in precursor fibres, before being further reckoned with another important role in structuring the micro-channels during the concurrence of phase inversion and viscous fingering phenomenon. However, it has been little linked to the sintering process, and consequently fully burnt off before the actual sintering of ceramic particles occurs, namely normally sintering.

In terms of sintering ceramic membranes using a normal sintering process, it has been acknowledged that the sintering process is composed of 3 major steps [7], i.e. initial, intermediate and final sintering, with the parameters associated with the stages of sintering (for polycrystalline solids) listed in Table 1. As a result, pore size and porosity of most ceramic membranes are normally the function of two primary factors, i.e. particle size and sintering profile including temperature, heating/cooling rates and dwelling time etc. This is also considered as one of the major reasons that, a thin separation layer made of finer particles needs to be supported on another substrate (more than one layer with a gradient pore structure) made of bigger particles, in order for a higher permeation flux and lower resistance.

The phase inversion assisted process used to fabricate ceramic hollow fibre membranes has allowed the single-step formation of a unique asymmetric structure consisted of a thin sponge-like layer (separation layer) supported on a finger-like layer with a plurality of micro-channels inside. Mass transfer resistance is thus substantially reduced due to the presence of micro-channels of this type, in contrast to conventional symmetric substrate

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structure. However, water permeation of such membranes is still largely dependent on pore size and porosity of the top/outer separation layer, due to the normal sintering conditions applied.

In this proof-of-principle study, a new controlled sintering process is developed to improve water permeation by using the continuous polymer phase (PESf) as a pore structure "stabilizer". Instead of being burnt off in the normal sintering process, the PESf phase is first thermally treated in static air, followed by conversion it into carbon in an oxygen free environment, together with the sintering of alumina particles at high temperatures. As a result, the drop in membrane porosity is not solely a factor of temperature due to presence of carbon around alumina particles. As such, an improvement in the membrane porosity and reduction in defects formation can be achieved at possibly a higher temperature when compared with normal sintering. Furthermore, the original concept of using the polymer phase as a pore structure "stabilizer" can be used to design the pore structure of ceramic membranes made of other materials, in order for a higher water permeation flux.

2. Experiments

2.1. Materials

Aluminium oxide (Al_2O_3) powder of 1 μm (alpha, 99.9% metals basis, surface area 6–8 m^2/g) was purchased from Alfa-Aesar and was used as supplied. Polyethersulfone (PESf) (Radal A300, Ameco Performance, USA), dimethyl sulfoxide (DMSO) (HPLC grade, Rathbone), and Arlacel P135 (polyethylene glycol 30-dipolyhydroxystearate, Uniqema) were used as a polymer binder, solvent and additive, respectively. Tap water and de-ionized water were used as the external and internal coagulants, respectively.

Table 1
Parameters associated with the stages of sintering for polycrystalline solids [7].

Stage	Typical micro-structural feature	Relative density range	Idealized model
Initial	Rapid inter-particle neck growth	≤0.65	Two monosize spheres in contact
Intermediate	Equilibrium pore shape with continuous porosity	0.65–0.90	Tetrakaidecahedron with cylindrical pores of the same radius along the edges
Final	Equilibrium pore shape with isolated porosity	≥0.90	Tetrakaidecahedron with spherical monosize pores at the corners

Table 2
Sintering parameters for normal sintering and controlled sintering.

Temperature (°C)		Rate (°C/min)	Dwelling time (min)	Atmosphere	Sintering type
From	To				
RT	600	2	–	Static air	Normal sintering
600	600	–	120		
600	1450	5	–		
1450	1450	–	240		
1450	RT	3	–		
RT	400–600	5	–	Static air (1st step)	Controlled sintering
400–600	RT	5	–		
RT	1450	5	–	N2 (2nd step)	
1450	1450	–	240		
1450	RT	3	–		
RT	800	5	–	Static air (3rd step)	
800	800	–	120		
800	RT	3	–		

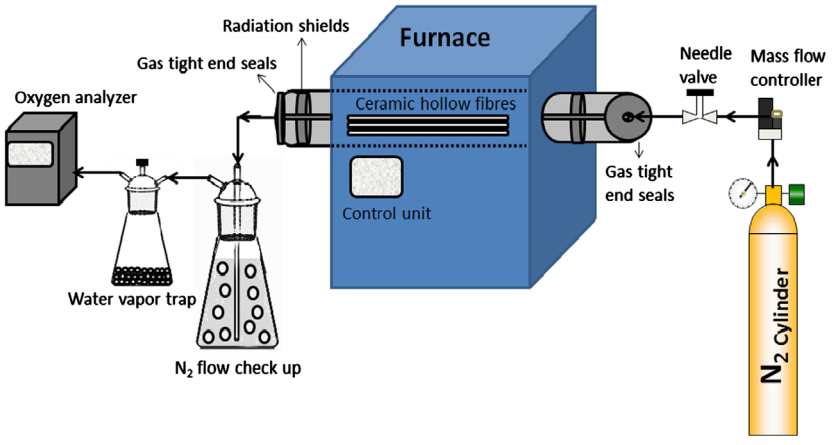

Fig. 1. Schematic diagram of experimental set-up for controlled sintering.