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Short Communication

# A phase-inversion casting process for preparation of tubular porous alumina ceramic membranes

Zhiwen Zhu [a,b], Jin Xiao [c], Wei He [d], Tsinghai Wang [a], Zhaoling Wei [b], Yingchao Dong [a,*]

[a] *CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, PR China*
[b] *Key Laboratory of Processing and Testing Technology of Glass & Functional Ceramics of Shandong Province, School of Materials Science and Engineering, Qilu University of Technology, Jinan, PR China*
[c] *Changzhou Institute of Technology, Changzhou, Jiangsu, PR China*
[d] *Department of Building and Real Estate, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*

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**Abstract**

In this study, a phase-inversion casting method with the self-designed forming mold and preparation route was proposed for preparation of tubular ceramic membranes. Thermal and sintering behaviors of as-prepared green tubular membranes were investigated. The results show that the significant weight loss occurs between 400 and 600 °C and three shrinkage stages appear in sintering process. Pore size distribution, image analysis, porosity, mechanical strength and gas flux were also studied to characterize the fabricated ceramic membranes. SEM images illustrate that the tubular membrane has a nearly homogeneous microstructure with good pore interconnect and uniform pore dispersion. With increasing of sintering temperature from 1500 to 1600 °C, the porosity decreases from 51.2 to 45.1% and the average pore size from 0.79 to 0.71 μm, while the flexural strength increases from 22.2 to 41.5 MPa. All these properties clearly suggest the practicability of the phase-inversion casting process to prepare tubular ceramic membranes.


*Keywords:* Ceramic membrane; Tubular membrane; Alumina; Phase inversion

## 1. Introduction

Ceramic membranes exhibit several advantages over their polymeric counterparts, such as high thermal stability at elevated temperatures, excellent chemical resistance in more corrosive environments and good mechanical properties [1,2]. Porous ceramic membranes have received intensive attentions in the past decades because of their successful applications as separation media for molten metal, hot gases and liquid filtration processes, catalyst supports and electrodes in fuel cells [3–7]. Alumina, zirconia, titania and silica are usually chosen as principle raw materials for commercialized ceramic membranes preparation. Generally the ceramic membranes possess an asymmetric structure consisting of a thick support membrane and a thin top-layer membrane. The support membrane is a key component of asymmetric ceramic membrane. This is because that it not only provides sufficient mechanical strength and low permeation resistance, but also possesses a smooth surface allowing a thin membrane layer to deposit on it without the introduction of defects. Beside, the support membrane also determines the membrane configurations, which play an important role in integration of a membrane module [8–10].

Currently, three main ceramic membrane configurations, flat membrane, tubular membrane and hollow fiber membrane are available in the market. Tubular membrane instead of flat membrane is recommended in separation application due to its several advantages in membrane modules: (a) high membrane surface area per unit of module volume. (b) Flow profiles through tubes are better defined with less risk of dead zones. (c)

* Corresponding author at: Ceramic Membrane and Environment Material Group, CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, PR China. Tel.: +86 592 6190790; fax: +86 592 6190977.
*E-mail address:* ycdong@iue.ac.cn (Y. Dong).

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Better match to existing reactor concepts often based on tubular structures [11]. Nowadays tubular membranes have been mainly used in some separation processes. Jedidi et al. [12] elaborated tubular ceramic microfiltration membranes for treatment of wastewater. Wang et al. [13] successfully prepared a tubular $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane and studied its oxygen permeation properties. Extrusion and casting are two popular techniques to fabricate tubular porous ceramic membranes. The extrusion technique is widely used for industrial manufacturing of various tubular ceramic membranes due to the continuous and mass production [14,15], but the ceramic membranes obtained by this method are usually possessing low porosity and coarse surface. Casting techniques, such as gel-casting, centrifugal casting and freezing casting, cost a little more than extrusion but are more capable for fabricating high quality tube with a homogenous packing layer and a smooth surface [16,17]. Gu et al. [18] fabricated porous YSZ ceramics using the gel casting method, with an open porosity of 33.1–50.3%, mean pore size of 0.66–0.98 μm and the nitrogen permeability of 215–438 $m^3\ m^{-1}\ bar^{-2}\ h^{-1}$. Alumina tubes of diameters of 8 and 20 mm, respectively with gradient porosity and smooth inner surface were successfully fabricated using centrifugal casting by Kim [19].

Phase inversion method is an emerging method for fabricating porous ceramic membranes especially those with hollow fiber geometry. For instance, Zhang et al. [20] and Fang et al. [21] have, respectively, reported the fabrication of porous silicon nitride and alumina hollow fiber membranes by phase inversion method. Recently tape casting method based on phase inversion has also been demonstrated to fabricate porous ceramic wafers [22,23]. Despite of these successes, few relevant studies toward the fabrication of tubular porous ceramic membrane via phase inversion process can be found in literature. In this work, a self-designed phase-inversion casting process is developed and applied to fabricate the tubular porous alumina ceramic support membrane. The most significant contribution of this work is that we propose a new and simple route to prepare tubular ceramic membrane, by which high-porosity tubular alumina membranes with moderate flexural strength were constructed.

## 2. Experimental

### 2.1. Membrane preparation

The porous tubular alumina membranes were prepared by the phase-inversion casting method. The whole preparation procedure was schematically shown in Fig. 1. The polyethersulfone (PESF, Gafone 3000P, Solvay Advanced Polyers) and polyvinylpyrrolidone (PVP, K30, Sinopharm Chemical Reagent Co., Ltd.) were completely dissolved into N-methyl-2-pyrrolidone (NMP, CP, Sinopharm Chemical Reagent Co., Ltd.) by ball-milling for 2 h using the planetary ball mill, resulting in a polymer solution containing 16.5 wt% PESF, 2.5 wt% PVP and 81.0 wt% NMP. A certain amount of alumina powders (97% purity, Tiantai, Henan Province, China) were added into the above polymer solution and then ball-milled again to obtain a homogenous suspension. Prior to casting, as-prepared suspension was degassed for 15 min to prevent the generation of the large cavities due to air bubbles in green tubular membrane.

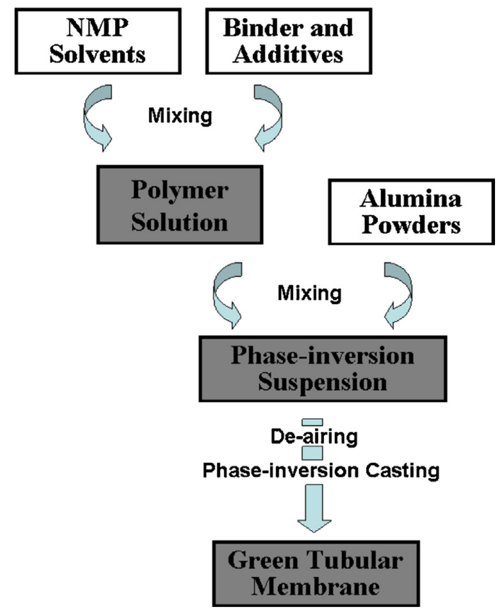


Fig. 1. Flowchart of the fabrication procedure of tubular ceramic membranes.

Fig. 2 presents the procedures of the phase-inversion casting technique for tubular membrane fabrication. First, degassed suspension was poured into a homemade casting device, and then the device was placed on water surface and kept in contact with water (Fig. 2A). After that, we pushed the piston into water at a certain speed, following that the suspension underwent the phase-inversion process and incompletely solidified in water (Fig. 2B). The partial solidified tubular membrane was then immersed in water for 48 h for further solidification (Fig. 2C). Finally the green tubular membrane was obtained after being taken off from the piston (Fig. 2D). After drying in an oven, the green tubular membrane was heated and cooled at a rate of 2 °C $min^{-1}$ in the high temperature box furnace (KSL-1700, Kejing Materials Technology Co., Ltd.), and dwelled at the highest temperature for 120 min.

To compare with the support membranes fabricated by a pressure forming technique, the disk and rectangular membranes were prepared by cold pressing method. The disk membranes were used to investigate the pore properties and the mechanical strength measurement was functioned on the rectangular membranes. The alumina powers with polyvinyl alcohol (PVA, Sinopharm Chemical Reagent Co.) blinder were uniaxially pressed under 200 MPa into disks with a diameter of 20 mm and rectangles with a dimension of 40 mm × 7 mm × 2 mm in the cylindrical and rectangular mold, respectively. The green samples were sintered at 1500, 1550 and 1600 °C for 120 min with a heating and cooling rate of 2 °C $min^{-1}$.

### 2.2. Characterization

The particle size distribution of the used alumina powders was detected by the laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd.) using water as dispersing medium.