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Preparation of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ hollow fibre membranes: Study on sintering processes

Yutie Liu, K. Li *

Department of Chemical Engineering and Chemical Technology, Imperial College London, University of London, South Kensington, London SW7 2AZ, UK

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Abstract

In this study, sintering processes, as one of the critical steps in ceramic processing responsible for final shape and characteristics of products, have been investigated using hollow fibre precursors prepared from a mixed proton/hole conducting material of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ (SCYb). The hollow fibre precursors were spun via a phase inversion method using a polyethersulfone (PESf)/N-methyl-2-pyrrollidone (NMP) solution system, which is often used in making polymeric membranes. In order to understand influences of the sintering process on the hollow fibre membranes, some sintering parameters such as sintering temperature, heating rate and sintering time have been investigated. The shrinkage and weight loss of the hollow fibres during the sintering processes have been measured at different calcination temperatures and the surface morphology of resulting hollow fibres has been investigated using scanning electron microscopy (SEM).

Keywords: Perovskite material; Hollow fibre membrane; Sintering process

1. Introduction

Recently, membranes with mixed ionic-electronic conducting abilities have attracted great research interest for their potential applications in chemical and electrochemical industries, especially in application of methane conversions [1–3]. One of the advantages of using such a mixed conducting membrane is the structural simplicity as no electrodes and external electric loadings are required compared to pure ionic (oxygen ion or proton) conducting membranes. Many studies have been conducted using either oxygen permeable material, such as, $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\alpha}$ (LSCF) [4-5] or hydrogen permeable materials, such as $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ (SCYb) [6–10]. Most of the research on the mixed-conducting ceramic membranes allowing permeation of oxygen or hydrogen focused on perovskite disk shaped membranes because preparation of these dense and defect free ceramic membrane by a press/sintering method is currently available. However, the disk-shaped membrane has a very limited effective area and in addition, up to millimeters thickness of these disk-shaped membranes would impose large mass transfer resistance. Although the thickness of the disk membrane could be reduced by depositing a thin top-layer on a porous support [8], for the prospective of industrial applications, hollow fibre membranes are still preferable compared to the disk shaped membranes. Liu et al. [9] first developed the SCYb hollow fibre dense membranes intended to use in methane coupling reactions to produce C_2 products. Their results showed an exciting possibility in developing ceramic hollow fibre membranes using a combined phase inversion and sintering method. However, performance of the module made from these hollow fibres was not very ideal due to the inadequate mechanical strength of the membranes, especially when the modules were operated at elevated temperatures.

There are many factors governing the fabrication of ceramic membranes. The sintering process plays a prominent role, since almost all the ceramic precursors must be fired at elevated and properly controlled temperatures in order to ob-

* Corresponding author. Tel.: +44 207 5945676; fax: +44 207 5945629.
E-mail address: kang.li@imperial.ac.uk (K. Li).

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tain its mechanical strength and microstructures with desired properties [11–16].

The objective of this study is concerned with the sintering processes. It is intended to observe how the sintering processes take place and influence the microstructural evolution of the hollow fibres prepared from a SCYb perovskite-type material. The effect of sintering temperature and sintering time on the microstructure-related characteristics including surface morphology, grain growth and pore evolution or elimination has been investigated.

2. Experimental

2.1. Materials

$SrCe_{0.95}Yb_{0.05}O_{2.975}$ (SCYb) powders prepared using a sol–gel method [10] were used as the hollow fibre material. Polyethersulfone (PESf) (Udel) and N-methyl-2-pyrrollidone (NMP) (>99%, Acros) were used to prepare spinning solutions. Polyvinlpyrrolidone (PVP K90) was used as an additive. Tap water was used as both the bore liquid and external coagulant.

2.2. Sintering processes

The hollow fibre precursors were prepared using a phase inversion method described elsewhere [9] and were dry-treated at about 25 °C before sintered in a furnace. The heating rate was of 2–5 °C/min applied during all the sintering processes. The sintering temperature is up to 1600 °C. The linear shrinkage and the weight loss of hollow fibres were measured and calculated after calcined at different temperature for different time. An average value was taken from three samples measured for each condition. The effect of sintering on surface morphology of the fibres was investigated using SEM.

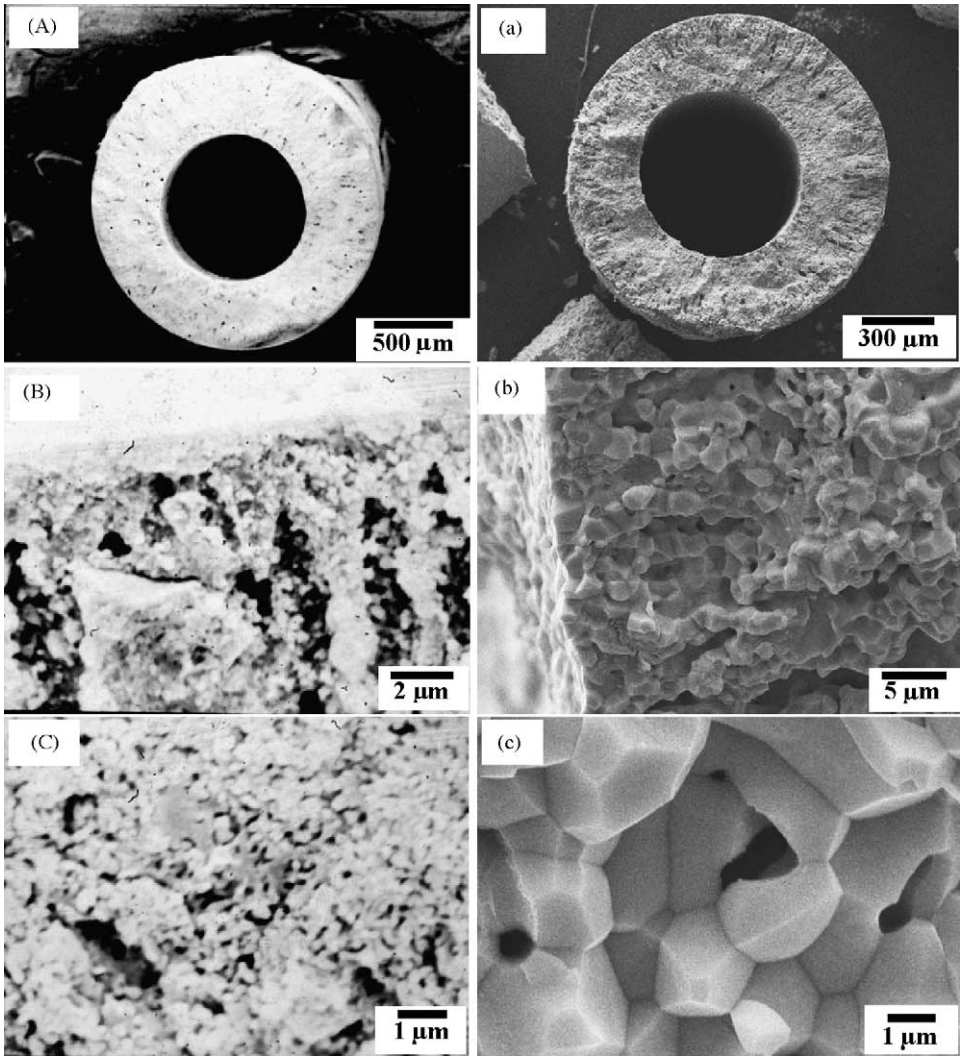

Fig. 1. SEM photographs of the cross-sectional structures of SCYb hollow fibre membranes (before sintering: (A) whole cross-section, (B) outer layer and (C) middle part) and (after sintering: (a) whole cross-section, (b) outer layer and (c) middle part).